THE REMOVAL OF MANGANESE IN DRINKING WATER

by

David A. Weakley II

Bachelor of Science, University of Pittsburgh, 2007

Submitted to the Graduate Faculty of

Swanson School of Engineering in partial fulfillment

of the requirements for the degree of

Master of Science

University of Pittsburgh

2009

UNIVERSITY OF PITTSBURGH

SWANSON SCHOOL OF ENGINEERING

This thesis was presented

by

David A. Weakley II

It was defended on

September 11, 2009

and approved by

Dr. Willie Harper Jr., Associate Professor, Civil and Environmental Engineering

Dr. Jason Monnell, Research Assistant Professor, Civil and Environmental Engineering

Dr. Stanley States, Water Laboratory Manager, Pittsburgh Water and Sewer Authority

Thesis Advisor: Dr. Leonard Casson, Associate Professor, Civil and Environmental Engineering

THE REMOVAL OF MANGANESE IN DRINKING WATER

David A. Weakley II, M.S.

University of Pittsburgh, 2009

Removing manganese while controlling the amount of disinfection byproducts formed in a drinking water plant and distribution system is a delicate balancing act. Currently the Stage 2 Disinfectants and Disinfection Byproduct Rule (Stage 2 DBPR), established by the United States Environmental Protection Agency (EPA), is designed to improve drinking water quality and provide additional public health protection from disinfection byproducts. Many drinking water systems will not be able to comply with the Stage 2 DBPR unless changes are made to their treatment and distribution systems [USEPA, 2007]. With compliance issues threatening, water treatment utilities across the nation are using or at least considering any means necessary to minimize disinfection byproducts.

Pittsburgh, Pennsylvania like many water utilities experiences elevated levels of iron and manganese in their drinking water. The most common and arguably the most effective means of removing iron and manganese is prefilter chlorination. Here, chlorine is introduced to water at the top of the filter and oxidizes the metals in solution to a solid state, after which, iron and manganese are removed on multimedia filters. The major water treatment utility concern was that prefilter water with elevated amounts of TOC (disinfection byproduct precursor) is being dosed with chlorine before the filters have a chance to remove the excessive organic matter. The

least amount of organic matter combined with the lowest chlorine dose necessary for metals removal and disinfection should create the lowest concentration of trihalomethanes.

The Pittsburgh Water and Sewer Authority (PWSA) devised and completed bench, pilot and full plant-scale experiments testing alternative methods of manganese removal. Novel technologies such as prefilter hydrogen peroxide and prefilter sodium permanganate oxidation were both tested in bench and pilot scale experiments. Bench-Scale studies utilizing ferric sulfate as a primary coagulant were conducted to determine the degree of manganese contamination compared with use of ferric chloride, PWSA's current coagulant. Prefilter chlorination and the effects on trihalomethane formation were also extensively studied.

The purpose of this research was to determine the optimal treatment approach that permits adequate removal of manganese, to prevent discoloration of finished water in the distribution system and produce the lowest concentration of disinfection byproducts, and therefore the safest water at the tap.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGMENTS

First, I would like to thank Dr. Leonard Casson and Dr. Stanley States. I could not have completed this research project without their help and guidance. To Dr. Casson, I want to thank you for your real world teaching style, knowledge of the field and the ability to differentiate the academic from the practical. He was a great professor and advisor who instilled the love of teaching in me. To Dr. States, who has wrestled with excessive manganese levels in the Allegheny River since he began working at PWSA, thank you for having and endless supply of innovative solutions and alternatives to problems that have plagued drinking water plants for decades and of course, thank you for your entertaining anecdotes.

In addition, many thanks to Dr. Jason Monnell and Dr. Willie Harper of the University of Pittsburgh for serving on my committee and their participation. Dr. Monnell has taught me invaluable lessons in correct laboratory procedures as well as given me a greater appreciation for chemistry. Before working with him, I tried to avoid chemistry related projects and problems, now I look to them as a challenge. Dr. Harper's exciting and relaxed teaching style has made many of the more difficult concepts in environmental engineering easy to grasp and hard to forget. I strive to be as great a teacher as Dr. Harper was to me.

Thanks to PWSA for their time and equipment for the research, especially Gina Cyprych, Mark Stoner, Jay Carroll, and Faith Wydra. Gina, thank you for keeping Stanley organized and helping me set up every experiment no matter how much "real work" you had to do. Mark,

thank you for running endless samples on the gas chromatography mass spectrometer and Jay, thanks for never giving me a hard time about the extensive metal tests that this research required and keeping me occupied with bike talk. And Faith, thank you for running a seemingly endless amount of wet chemistry samples.

Special thanks to my fiancée, Liz Kearns, who weathered the late nights and early mornings of writing and research. Without your love, support, patience, and distractions, I would not have been able to finish this thesis. We truly are a great pair, capable of conquering all sorts of odds. Thank you to my loving and supportive parents, Dave and Toni Weakley, who have always guided the boat and encouraged me to put that extra effort. Thanks to my brother Clayton who gave me endless opportunities to take my mind off of research and to not forget to have fun. Last but not least thank you to Brittany Hohman and the rest of the Chesterfield crowd. You have all given me support and guidance throughout this project, letting me vent about frustrations and setbacks. You have put situations back into focus and helped me to persevere. Thank you all.

1.0 INTRODUCTION

The Pittsburgh Water and Sewer Authority (PWSA) is the drinking water utility for the City of Pittsburgh, Pennsylvania. The storage and distribution system contains large changes in elevation and subsequently contains 15 pressure zones. Within these 15 pressure zones, water flows through approximately 1,200 miles of distribution mains. There are five finished water reservoirs that hold a combined volume of over 400 million gallons of treated water. In addition to the four reservoirs, there are 10 finished water storage tanks, 11 pumping stations, and seven (soon to be ten) chlorine booster stations. Because the utility has only one water source, one drinking water treatment plant, and no substantial backup finished water supply available from neighboring utilities, PWSA must rely on several days of stored water for emergencies. PWSA serves approximately 250,000 customers in the city of Pittsburgh and surrounding areas. Due to increasingly stringent regulations, controlling disinfection byproducts are a primary concern of many drinking water systems in the United States. In addition to those concerns, PWSA is also trying to remove manganese from the finished water prior to storage and distribution [States, 2009].

In 2006, the United States Environmental Protection Agency (EPA) enacted the Stage 2 Disinfectants and Disinfection Byproduct Rule (Stage 2 DBPR) to further monitor concentrations of disinfection byproducts (DBP) in water treatment and distribution systems. Two prominent components of DBPs are trihalomethanes (THMs) and haloacetic acids (HAA).

The formation of these compounds increase when either the dose or contact time of chlorine is increased. Elevated amounts of organic matter present during chlorination may also increase DBP formation. Beginning in 2005, PWSA took a preventative measure against DBP formation with enhanced coagulation [States, 2009]. Enhanced coagulation is a method of lowering the pH and increasing the coagulant dose during the rapid mix stage to promote the flocculation of organic matter for removal by sedimentation.

Manganese is a metal found naturally in the Allegheny River which is the source water for PWSA drinking water. Manganese levels in drinking water are regulated by the EPA as a secondary contaminant under the Safe Drinking Water Act. Secondary pollutants are not considered health hazards, but are regulated for aesthetic reasons. Elevated levels of manganese will give drinking water a "tea" color and a metallic odor and taste. The secondary maximum contaminant level (MCL) for manganese in finished drinking water is 0.05 mg/L.

A commonly used treatment method is to add potassium permanganate ($KMnO_4$) at the head of the treatment plant to oxidize the Mn^{2+} to manganese dioxide (MnO_2). Manganese dioxide is a precipitate that can be removed through multimedia filtration. PWSA uses $KMnO_4$ to oxidize the dissolved manganese in the raw water, however with enhanced coagulation and the subsequent lower pH; $KMnO_4$ yields additional Mn^{2+} ions. Free chlorine, in the form of sodium hypochlorite, is used to oxidize manganese ions to manganese dioxide. Sodium hypochlorite oxidizes Mn^{2+} regardless of the pH and is easily added into the settled water before the multimedia filters. A concern with the use of chlorine as a manganese oxidizer is the possible additional DBPs the free chlorine may create when combined with organic matter in the settled water.

The solution to the problem of removing manganese while still being compliant with disinfection byproduct regulation lies in treatment optimization. This can involve use of a coagulant with less manganese contamination, dosing permanganate before the filters instead of chlorine, and finally increase the pH prior to filtration.

1.1 OBJECTIVES OF THE RESEARCH

The overall objective of this research is to explore methods to better remove manganese while reducing formation of disinfection byproducts. In accordance with EPA's Stage 2 Disinfectants and Disinfection Byproducts Rule, the levels of THMs and HAAs need to be minimized. Although free chlorine provides adequate oxidation of manganese, the DBP formation is harmful to human health and is in violation of the EPA. The following alternatives for manganese removal were explored during this research:

- Chlorine and Hydrogen Peroxide Jar Tests: Hydrogen peroxide was added to settled water to oxidize iron and manganese. After, the water was filtered and dosed with sodium hypochlorite (free chlorine) to simulate filtration and disinfection.
- Hydrogen Peroxide at Varying pH Levels: After the original hydrogen peroxide bench-scale study, a new experiment was devised to see the effect hydrogen peroxide's oxidation ability in an elevated pH environment.
- Ferric Chloride and Ferric Sulfate Jar Test: PWSA's current coagulant is ferric chloride. Ferric chloride was evaluated and contained elevated levels of manganese contamination. When ferric chloride is used, the manganese levels measured after coagulation are greater than the raw water. Ferric sulfate, as a coagulant, was shown

in studies to contain less manganese contamination than ferric chloride. Both ferric chloride and ferric sulfate were compared with and without potassium permanganate to determine which coagulant contained more manganese contamination in a bench-scale study.

- Liquid Permanganate Jar Test with Varying Dosage: Potassium permanganate is currently used at the head of the treatment works at PWSA to oxidize and aid in the removal of manganese. Potassium permanganate ($KMnO_4$) is a solid crystal that is dissolved in water. Difficulties arise in handling and dosing the chemical due to its crystalline nature. However, sodium permanganate ($NaMnO_4$) 20% stock solution is fully dissolved and creates no harmful dust when handling. Bench and pilot-scale studies were completed to evaluate the effectiveness of dosing sodium permanganate before the filters to oxidize and remove reduced manganese.
- Elevated pH Prefilter Chlorine and Permanganate Jar Tests: Currently, PWSA is using potassium permanganate to aid in manganese oxidation and removal. Potassium permanganate is more effective with a higher pH level. However, with enhanced coagulation it is necessary to lower the pH to remove organics in the flocculation and sedimentation stage. The bench-scale experiments here examine the effects of lower doses of prefilter chlorine and permanganate used to oxidize iron and manganese in an elevated pH environment. The elevated pH prefilter chlorine and permanganate jar tests study the effects of raising the pH after the enhanced coagulation stage. Both the prefilter chlorine and the sodium permanganates effectiveness was monitored with respect to pH level.

- Prefilter Chlorination THM study: Prefilter chlorination works very well for removing iron and manganese on the filters. The concern of water treatment utilities is that there will be an increase in disinfection byproducts due to the chlorine being introduced at a stage with higher disinfection byproduct precursors (TOC and UV 254 absorbance). The prefilter chlorination plant-scale study is designed to determine the effect of prefilter chlorination with respect to formation potential.
- Chlorine Spike Experiment: The prefilter chlorination study was a plant-scale study and had many uncontrollable variables. However, the chlorine spike experiment however was a bench-scale experiment created to test the THM formation potential on water that has been prefilter chlorinated and water that has not. The experiment was developed because the chlorine dosing system in the clearwell of PWSA's treatment plant is a residual based system. When chlorine is dosed before the filters, there is still a residual by the time the water flows to the clearwell. In the clearwell, less chlorine is added to create the desired residual for disinfection. If there is no prefilter chlorination, a greater dose of chlorine in the clearwell is added to attain the desired residual for disinfection and distribution. In the chlorine spike experiment, water samples are collected from the top and bottom of the filter; both samples are dosed with the same amount of free chlorine. Trihalomethane formation potential after seven days is determined, thus concluding if prefilter chlorination affects THM formation.
- Disinfection Byproduct Precursor Plant Profile: Organic matter is measured by total organic carbon (TOC) and by UV 254 spectroscopy. These two tests measure disinfection byproduct precursors because they gage the concentration of organic

matter. Organic matter can react with halogens such as chlorine to form DBPs. Through different physical and chemical process of the treatment works, organic material is removed. A disinfection byproduct precursor profile was created to determine how effective each unit processes was at removing organic matter measured by both TOC and UV 254 absorbance.

- Liquid Permanganate Pilot Study: The back half (settled water to filters) of PWSA's pilot plant was used to scale up the sodium permanganate bench-scale experiment to a pilot-scale experiment. Flow rates through the filters were adjusted to replicate PWSA plant loading rates. Sodium permanganate was dosed from a day tank at a rate specified by jar tests run earlier in the week.

2.0 BACKGROUND

2.1 PITTSBURGH WATER & SEWER AUTHORITY

The Aspinwall Water Treatment Plant, owned and operated by Pittsburgh Water and Sewer Authority (PWSA), is located on the north bank of the Allegheny River. The plant intakes draw water from the Allegheny River for treatment. The goal of PWSA is to provide high quality drinking water to customers with sufficient pressure at minimal cost to Pittsburgh residents [Daley, 2007].

2.1.1 Capacity and Demands of the Distribution System

The PWSA distribution system is robust with sufficient pumping, storage, and pipe network capacity to meet current and future population, fire flow, and emergency demands. The distribution system has 10 pump stations within the 15 pressure zones. The elevation changes and large service area provide for great variability within the system and the vast service area with multiple storage facilities creates long detention times in the system [Daley, 2007].

The system demand for PWSA is a function of water usage patterns as well as temporal and diurnal variations. The PWSA system has variations in water demands depending on industrial and commercial usage, seasons, weather, and community practices. The Allegheny

River provides a continuous source of water to meet these demands; therefore, water scarcity is not a concern for Pittsburgh as it is in some other American cities [Daley, 2007].

The PWSA treatment system includes two treatment facilities, the Aspinwall Water Treatment Plant (AWTP), which uses conventional coagulation, flocculation, sedimentation, filtration, disinfection treatment and the Highland No. 1 Membrane Filtration Plant (membrane plant). The AWTP is located in Pittsburgh near Aspinwall, PA on the north shore of the Allegheny River. The Aspinwall treatment plant is the primary drinking water treatment facility for the Pittsburgh storage and distribution system, producing on average 70 million gallons per day (MGD). The 70 MGD of drinking water produced by PWSA services over 250,000 residents in the greater Pittsburgh area, and as many as 200,000 commuters who come into the city each day for work, school, business, and recreation. Depending on demand, AWTP may treat up to 100 MGD (design and permitted capacity). The membrane plant is located in Highland Park, a neighborhood within the city of Pittsburgh. The membrane plant treats the effluent from the Highland No. 1, an uncovered finished water storage reservoir. The membrane plant has the capacity to filter and disinfect 26 MGD [Daley, 2007].

Pittsburgh's drinking water system was significantly impacted in the 1980s by the collapse of the United States steel industry. Like many other cities in the northeast United States, Pittsburgh was prosperous during the industrial revolution. However, today Pittsburgh does not have the manufacturing plants and industry that once created large water demands. Instead, Pittsburgh is focused on converting these industrial properties into residential and commercial areas. The future of Pittsburgh lies in healthcare and services, technology, and education [Flaherty, 2002]. In addition to economic changes, Pittsburgh's population continues to decline. The declining population is another factor in excess water production capabilities of

PWSA. The above factors contribute to the fact that the stored volume of water PWSA manages is large compared to the daily demand. Although it should be noted that the distribution system is aging and encounters water main breaks, especially during the winter months. The PWSA stored water is imperative to maintain service to customers due to system reliability problems. Since the utility operates just one primary treatment plant on one river, and since none of the surrounding interconnected public water systems are able to supply sufficient volumes of water to backup the PWSA supply, Pittsburgh's contingency for emergency situation is stored finished water [States, 2009].

2.1.2 Distribution and Pumping

Once water is filtered through the AWTP dual media filters, the water flows by gravity to the clearwell where it is chlorinated and fluoridated. The water leaves the clearwell through a common wet well where water is then drawn to one of two high service pump stations. The two high service pumping stations are Aspinwall and Bruecken Pump Station. Aspinwall Pump Station is located directly east of the clearwell. Water flows east to west through the clearwell, and Aspinwall Pump Station draws water back through an 84-inch pipe that runs along the bottom of the clearwell. Bruecken Pump Station is south of the clearwell, drawing water across the Allegheny River through two 72-inch suction mains [Daley, 2007].

In Figure 1, The Bruecken Pump Station (B) takes water from the clearwell (C) and lifts it to the Highland No. 1 and Highland No. 2 Reservoirs (1 & 2, respectively) influents (star balloons). The diamond balloons mark the locations where the water exits the reservoirs. The water, which exits Highland No. 2 Reservoir, goes directly into the distribution system because it is a covered reservoir. The Highland No. 1 Reservoir water is treated by the membrane plant

(M) before being discharging to the distribution system. The Aspinwall Pump Station pumps water directly to Fox Chapel and to Lanpher Reservoir. After water is lifted to one of the three primary reservoirs, water is pumped and/or gravity fed throughout the Pittsburgh system. Water flows from one storage facility to another to cover all of the pressure zones.

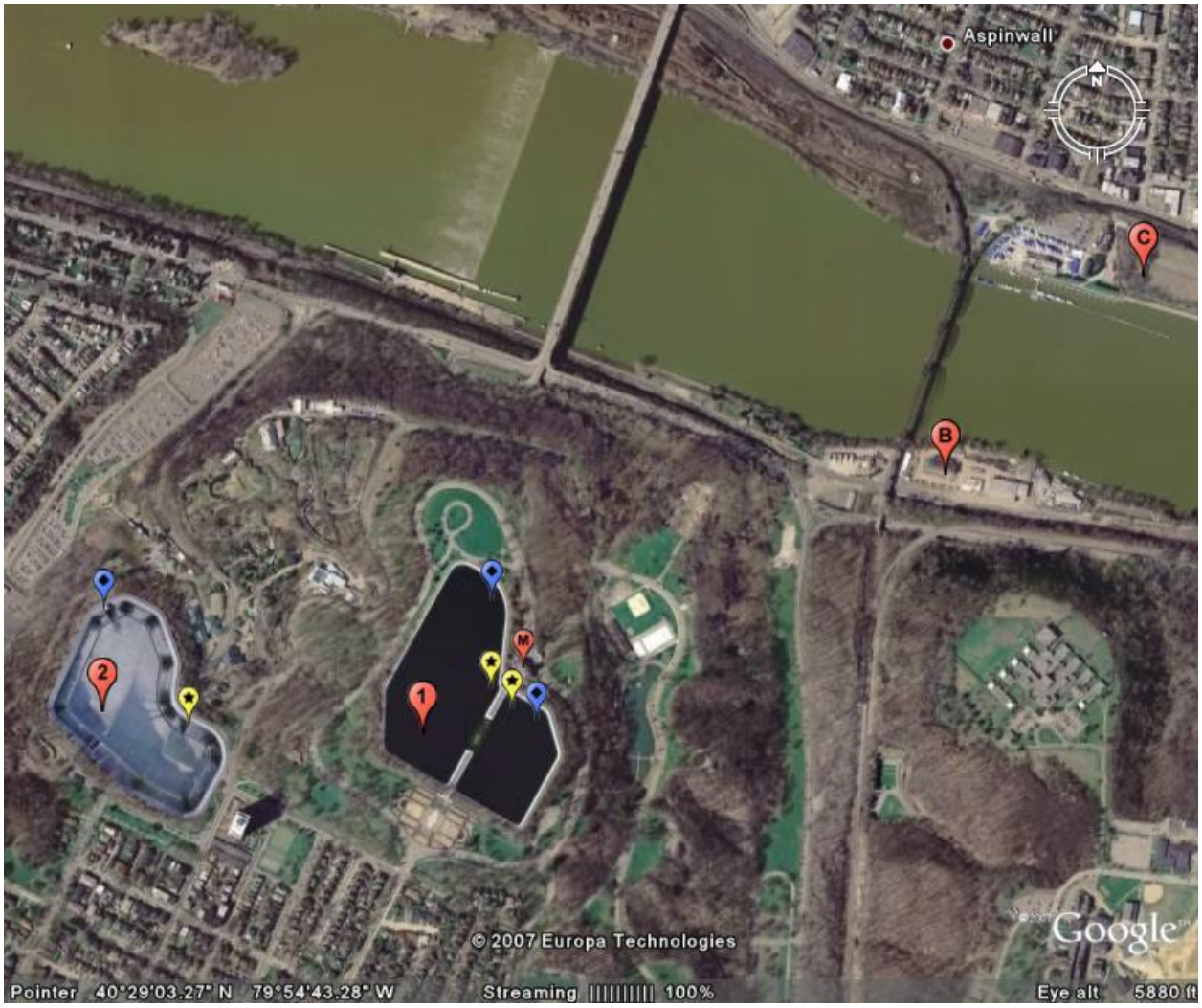

Figure 1. Figure 1. Highland No. 1 and No. 2 Reservoir Influent and Effluent Locations

(C) = Clearwell Outlet, (B) = Bruecken Pump Station, (1) = Highland No. 1 Reservoir, (2) = Highland No. 2 Reservoir, (M) = Membrane Plant, Yellow Balloons = Reservoir Influents, Blue Balloons = Reservoir Outlets. The distance between (C) and (B) ≈ 0.29 miles. The distance between the closest borders of (1) and (2) ≈ 0.17 miles

A schematic of how the water is pumped to the different storage facilities from the AWTP is displayed in Figure 2. Eight outlying pump stations are used to transfer water to higher pressure zones in the system, including Lincoln, New Highland, Herron Hill, Herron Hill Tank, Mission, Saline, Howard, and Fox Chapel Pump Stations. Millvale Borough, one of three

consecutive systems, which purchases water from PWSA, also has a pumping station that is currently not in service. The interconnection and pumping station operated by Millvale Borough is located on the 60-inch main leading from Lanpher Reservoir.

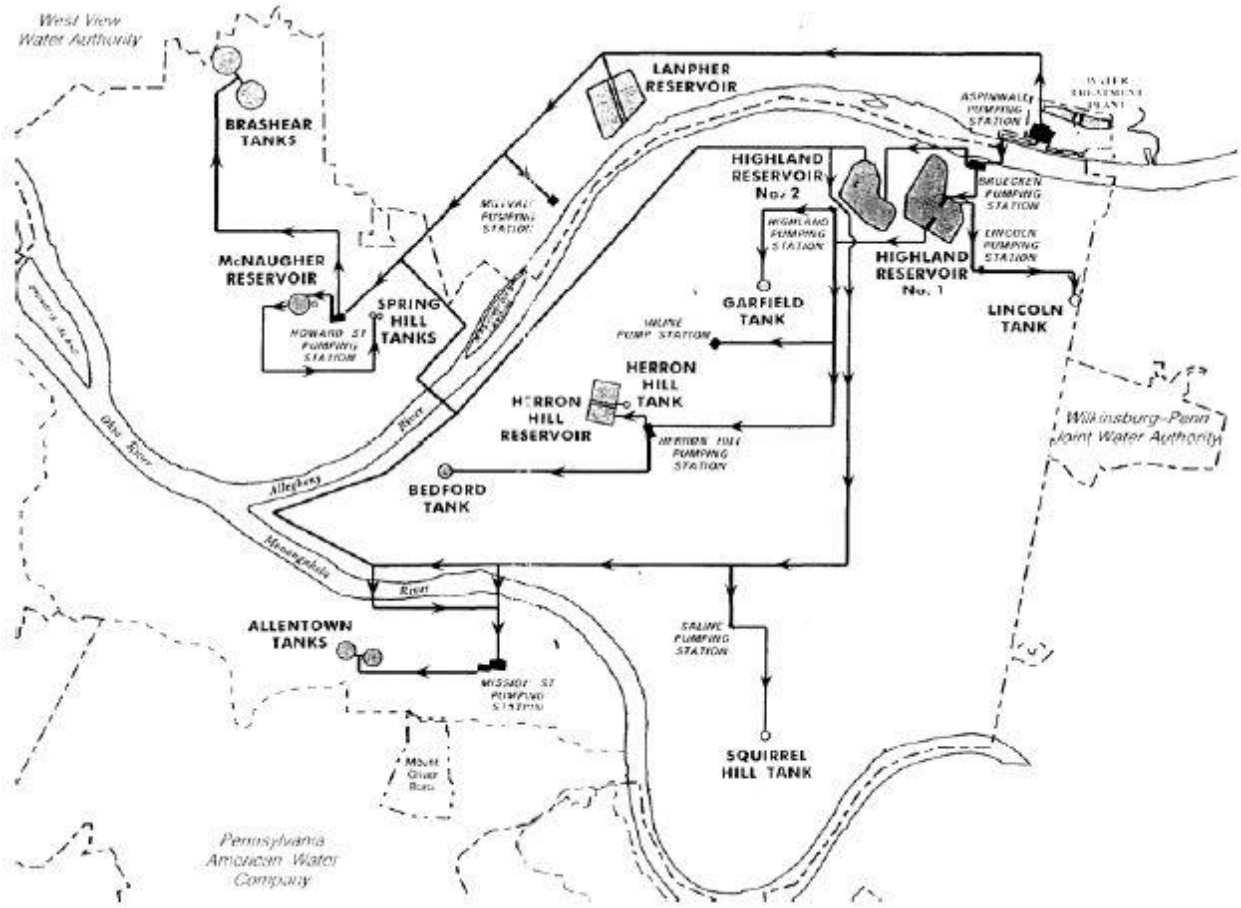

Figure 2. PWSA Water Storage Facility and Pumping Station Locations

2.1.3 Pressure Zones

PWSA has a distribution system including 15 pressure zones that are organized into the following super-systems:

- Highland No. 1 Super-system

    - Highland No. 1 Reservoir
    - Inline Pump Station
    - Lincoln Tank
    - Garfield Tank
    - Herron Hill Reservoir
    - Bedford Tank
    - Pressure Regulated Areas
        - Bloomfield Regulator
        - Highland Park/Garfield Regulator
        - Zoo Regulator
- Highland No. 2 Super-system
    - Highland No.2 Reservoir
    - Squirrel Hill Tank
    - Allentown Tanks
- Lanpher Super-system
    - Lanpher Reservoir
    - McNaugher Reservoir/Spring Hill Tanks
    - Brashear Tanks
    - Pressure Regulated Areas
        - McNaugher Regulator

The super-systems are centered on three primary reservoirs, Highland No. 1, Highland No. 2, and Lanpher Reservoir. The Highland No. 2 and Lanpher Reservoirs are at approximately

the same surface elevation; about 100 feet lower than the surface elevation in the Highland No. 1 Reservoir. Therefore, Highland No. 1 Super-system services the higher elevations and the Highland No. 2 and Lanpher Super-systems service the lower elevations. Connections between the Highland No. 2 (south of the Allegheny River) and the Lanpher (north of the Allegheny River) Reservoir Super-systems remained open until November 2006. These three river crossings were located at 26th Street, North Franklin Street, and Fort Duquesne Bridge. Now, the distribution system is operated as three isolated systems to facilitate control of disinfectant levels and formation of disinfection byproducts [States. 2009]

2.1.4 Finished Water Storage

Pittsburgh has a complex reservoir and water tower gravity fed system. PWSA storage facilities include:

- Reservoirs (storage basins or below grade)
    - Lanpher Reservoirs (2 cells)
    - Highland No. 1 Reservoir (2 connected cells)
    - Highland No. 2 Reservoir (1 cell)
    - Herron Hill Reservoir (2 cells)
- On-Ground Tanks (storage tanks at grade)
    - Spring Hill Tanks (2)
    - Brashear Tanks (2)
    - Allentown Tanks (2)
    - Squirrel Hill Tank (1)

    - Bedford Tank (1)
    - Lincoln Tank (1)
- Elevated Storage Tanks (storage tanks above grade)
    - Herron Hill Tank
    - Garfield Tank
- AWTP Secondary Sedimentation Basins (3)

These storage facilities provide sufficient water and pressure to the Pittsburgh distribution system during high and low demand periods. They also provide emergency flow for fires, water main breaks, power outages, and scheduled AWTP shut down periods. If the intakes to AWTP need to be closed due to a river spill or plant maintenance, the storage facilities can be filled to the operating capacity to service the distribution system. At full capacity, the ability of the storage facilities to service the distribution system is limited by the 26 MGD membrane plant [Daley, 2007].

The membrane plant services the Highland No. 1 Super-system, which has demands exceeding 26 MGD. Therefore, water is pumped directly to some of the Highland No. 1 Super-system areas from the AWTP. The secondary sedimentation basins, which are part of the AWTP process train, provide an addition 123 MG of stored water within the plant. When the intakes are closed, these secondary storage tanks assure that there will be sufficient finished water to pump to the three primary reservoirs and directly to the Highland No. 1 Super-system. PWSA has to rely on its stored water because there is no substantial backup finished water supply available from neighboring utilities. With the 15 pressure zones in the system, the reservoirs and elevated towers are able provide a constant pressure, via gravity feed, to customers with minimal

fluctuations during emergency situations such as power outages and water main breaks [Daley, 2007].

Flows patterns in the distribution system and levels in the reservoirs are continuously changing. The fluctuations of flow patterns are due to diurnal demand patterns and pumping protocols. This creates non-steady state hydrodynamic conditions through the distribution system. The majority of pumping for PWSA occurs during nights and weekends when electricity rates are lower and demand is low. Since the volume of water pumped is greater than the volume of water in demand, net storage increases. By Monday morning, the storage facilities are typically filled to their designated maximum level. Then, during the week, the levels in the reservoirs tend to drop due to deceased pumping. Keeping the reservoirs full allows PWSA to provide water with sufficient pressure to the distribution system during emergencies (e.g. power outages, fires, waterline breaks) [Daley, 2007]. From an AWWA and Economic and Engineering Services, Inc. (EES) literature review of finished storage water facilities [2002] prepared for the EPA, it was found that finished water storage facilities were historically operated at their maximum capacity, emphasizing hydraulic considerations. However, recent disinfection byproduct regulations focus attention on water quality considerations. Maintaining full storage facilities provides more storage capacity than is needed for non-emergency demands. Longer detention times for water created by fuller storage facilities results in the degradation of water quality. Therefore, PWSA has lowered the maximum operating fill levels of some of the storage facilities in effort to better utilize the existing water storage and maintain water quality [Daley, 2007].

PWSA's storage facilities pose a security risk since they are nodes for intentional water contamination. The tank enclosures, reservoir covers, and membrane plant are protective

barriers to guard against intentional water contamination. Until the mid 1990's, all of Pittsburgh's reservoirs were uncovered [Daley, 2007]. Then the amendment to the Pennsylvania Department of Environmental Protection (PADEP) Chapter 109 (Safe Drinking Water) of the Title 25 Environmental Protection document required PWSA to replace or cover the reservoirs [PADEP, 2004]. Now all of them, except one, are covered with a floating cover [Daley, 2007]. The exception was due to a public outcry to keep the reservoir uncovered for recreation.

Highland No. 1, Highland No. 2, and Lanpher Reservoirs are the three primary reservoirs with capacities of 117, 125, and 133 MG, respectively. Highland No. 1 Reservoir, located in Highland Park, consists of two basins that are connected by a shallow channel as shown in Figure 1. At one time, the reservoir consisted of two separate cells, however, the shared wall failed when taking water level down in one of the cells. This reservoir is the only Pittsburgh storage facility that remains uncovered. This reservoir is not baffled and there is one inlet and outlet in each cell. The geometry of Highland No. 1 is irregular, with the smaller, squarer basin to the east. During the week, Highland No. 1 Reservoir is visually inspected daily for contamination, vandalism, dead animals, operational readiness, etc [Daley, 2007]. The inspection protocol matches the AWWA and EES [2002] covered storage facility literature and research review which outline recommendations to complete daily or weekly physical inspections of storage facilities. All of the effluent from both basins of the Highland No. 1 Reservoir is treated through the 26 MGD membrane plant [Daley, 2007].

Highland No. 2 Reservoir is one large basin with one inlet and outlet. This 'L' shape basin, also shown in Figure 1, was covered and baffled in 1998 with a flexible polypropylene floating cover to comply with PADEP standards. Highland No. 2 is also in Highland Park, west of Highland No. 1 Reservoir. Water exits to the west of this basin through a chlorine house

where the chlorine residual is boosted with sodium hypochlorite. Since the installation of the cover, the inside of the reservoir has not been inspected for structural integrity or possible debris accumulation, although, the cover is visually inspected daily by PWSA personnel [Daley, 2007].

Lanpher Reservoir is located in Shaler Township between Etna and Millvale, PA. The reservoir was originally one basin, but was divided into two for Class 1 reliability. Both cells are trapezoidal in shape. Water flows in through a common channel, down the center of the two cells, from the northwest to southeast. The division structure at the end of the channel splits the influent into two cells. Water flows into the cells through a baffling structure that spans approximately half of the tank width. There is one outlet in each cell. The two effluent channels and one influent channel can be accessed in the chlorine house. Residual chlorine is added to the effluent channel to maintain a total chlorine residual of 0.40 mg/L throughout the distribution system. The two effluent channels are then connected into the 60-inch service main where the effluents are mixed together [Daley, 2007]. Like Highland No. 2 Reservoir, Lanpher reservoir was covered with a polypropylene cover in response to the Chapter 109 amendment to the Title 25 Environmental Protection document which required PWSA to replace or cover the reservoirs [PADEP, 2004]. Since the installation of the polypropylene covers, neither the Highland No. 2 nor the Lanpher Reservoir has been taken out of service for cleaning or inspection of structural integrity [Daley, 2007]. The three primary reservoirs are visually inspected daily from the perimeter, but the AWWA and EES [2002] review of finished water storage facilities listed recommendations of cleaning covered facilities at least every three to five years and uncovered reservoirs annually or bi-annually to maintain water quality in the storage facilities [Daley, 2007] The cleaning of covered facilities recommendation is not followed by PWSA [States, 2009].

2.1.5 Treatment Operations and Water Quality

PWSA operates a conventional 100 MGD drinking water treatment plant consisting of raw water screens, rapid mix, flocculation, flocculation, two-stage clarification, filtration and disinfection processes. In 2005, PWSA started enhanced coagulation, which was stated by AWWA and EES [2002] in a literature review prepared for the EPA on how the age of water effects quality in distribution systems, to be the best available technology specified in the Disinfectants and Disinfection Byproducts Rule for natural organic matter (DBP precursor) removal. This process improves the biochemical stability of the finished water and decreases water quality problems associated with aging water [Daley, 2007]. This quality improvement is the result of reduced organic matter and suppressed biological and chemical reaction rates in the stable water [AWWA and EES, 2002].

Currently, PWSA monitors the distribution system daily for disinfectant residual. This test ensures that the general distribution water quality is acceptable, with a total chlorine residual goal of 0.40 mg/L at all taps [States, 2009]. Typically, almost all the total chlorine residual is in the form of free chlorine [Daley, 2007]. PWSA also runs weekly composite chemical analysis on the finished water to determine turbidity, temperature, pH, alkalinity, hardness, carbon dioxide, chloride, calcium, magnesium, fluoride, sulfate, specific conductance, total solids, dissolved solids, and suspended solids [PWSA, 2006]. In addition, total metals analysis is conducted on the influent and finished water to determine the removal efficiency of iron, manganese, arsenic, lead, sodium, cadmium, silver, selenium, beryllium, zinc, chromium, copper, nickel, antimony, and thallium [PWSA, 2006]. The Allegheny River is rich in manganese and iron, due in part, to acid mine drainage in the surrounding Pittsburgh area. PWSA uses the oxidation/sedimentation/filtration processes for the removal of iron and

manganese, and other metals to decrease the levels released into the distribution system [Daley 2007].

The operations center for the Aspinwall Water Treatment Plant and pump stations is located in the operations building at the Aspinwall Plant. Built in 1969, the operations building provides office, laboratory, conference, mechanical, and storage space for administrative and operations usage. In the future, the membrane plant control center will be moved from the membrane plant to the AWTP. The majority of the AWTP equipment and distribution system is monitored continuously by a PWSA employee on computers and panels that relay the plant and distribution system status information. Every hour, the plant operators manually record readings from the system. These values include pump rates, storage tank elevations, and other treatment plant information. The recorded data provides valuable historical records on how the system was operating during a certain period [Daley, 2007].

A variety of chemicals are used during the water treatment process including potassium permanganate, powdered activated carbon, coagulant aid polymer, ferric chloride, lime, caustic soda, sodium hypochlorite, and soda ash. Post filtration, the finished water receives a hydrofluosilicic acid and additional sodium hypochlorite dose [Daley, 2007].

Below in Figure 3 is the typical process flow diagram for a surface water treatment plant. At PWSA, the raw water is pumped from the Allegheny River in Aspinwall, PA. Next the water flows through the bar screens and to the chemical dosing and rapid mix stage. The water flows into the flume where it coagulates and flocculates, next the water goes through secondary sedimentation in large basins across Freeport Road. The water then flows back to the top of the filter where it is dosed with filter aid and prefilter chlorine. After which, the water flows through anthracite, sand then gravel and on to the clearwell for disinfection.

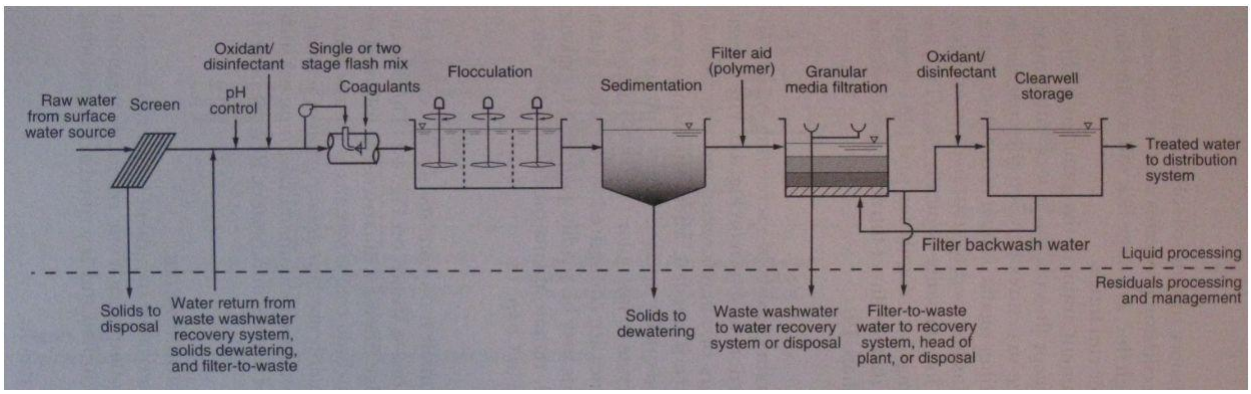

Figure 3. Process Train for Surface Water Sourced Drinking Water
[MWH, 2005]

Although there are background levels of fluoride in the source water, the Allegheny River. PWSA adds hydrofluosilicic acid as a 25 percent solution to finished water between the filters and the clearwell to raise the concentration. Fluoride is added to the water for dental health benefits. The dosage pump runs continuously and is adjusted once daily based on sampling results. The goal is to achieve a fluoride concentration of approximately 1.0 mg/L throughout the distribution system [Daley, 2007].

Sodium hypochlorite is used as PWSA's primary and secondary disinfectant. The finished water receives a primary dose of sodium hypochlorite at the entrance to the clearwell. Secondary disinfection is provided by continuous rechlorination systems. The systems are on/off controlled and placed throughout the PWSA distribution system. There is chlorine feed at the membrane plant to water entering the distribution system from Highland No. 1 Reservoir and seven chlorine booster stations located at outlets of the following facilities:

- Lanpher Reservoir
- New Highland Pump Station (influent to Garfield Tank)
- Highland No. 2 Reservoir
- Herron Hill Reservoir

- Brashear Tanks
- McNaugher Reservoir
- Bedford Tank

PWSA has built and is in the process of commissioning three additional booster chlorine stations to the outlets of the following facilities:

- Allentown Tanks
- Squirrel Hill Tank
- Lincoln Tank

The construction on the three additional chlorine booster stations is complete. PWSA is currently working on commissioning each booster station for setup. The additional three booster stations should allow PWSA to better control chlorine residual and DBP formation through the distribution system. Currently, the Allentown and Squirrel Hill Tanks are fed from Highland No. 2 Reservoir and Lincoln Tank is fed from Highland No. 1 Reservoir. High concentrations of chlorine are added at the effluents of these two primary reservoirs to assure adequate disinfectant residual through the secondary storage facilities and distribution lines to customer homes and businesses. The new booster stations will be paced by chlorine residual so lower concentrations of chlorine will need to be added at the primary reservoirs [States, 2009]. However, the residual pacing still does not guarantee predictable residual levels [AWWA and EES, 2002]. Chlorine residual will still change depending on flow patterns and chlorine demand in the water after the booster station. Therefore, PWSA may still incur periodic over and under dosages of chlorine [Daley, 2007].

2.1.5.1 Enhanced Coagulation

In an effort to better control disinfection byproduct formation, the EPA disinfectant disinfection byproduct rule requires that US surface water treatment plants whose influent and effluent waters meet a certain criteria practice enhanced coagulation. This treatment technique has shown to be effect in reducing natural organic matter and consequently disinfection byproducts [States, et al., 2002].

The term "enhanced coagulation" refers to the process of improving the removal percentage of disinfection byproduct (DBP) precursors in a conventional water treatment plant [USEPA, 1999]. The modifications include reduction of pH to levels of 5 to 6 during the coagulation process and or the use of higher doses of coagulants [States, et al., 2002]. "Enhanced softening" refers to the improved removal of DBP precursors by precipitative softening. The removal of natural organic matter (NOM) in conventional water treatment processes by the addition of coagulant has been demonstrated by laboratory research and by pilot-scale, demonstration-scale, and full-scale studies. Several researchers have shown that total organic carbon (TOC) in water, used as an indicator of NOM, exhibits a wide range of responses to treatment with aluminum and iron salts [USEPA, 1999].

At very low pH levels, positively charged products from hydrolysis yielded from metal coagulants neutralize negatively charged NOM and form insoluble complexes. Additionally, elevated doses of metal coagulants more effectively adsorb NOM onto the coagulation precipitates [States, et al., 2002]. Above explains the reasoning behind lowering the pH level and increasing the coagulant dose.

2.2 SAFE DRINKING WATER ACT

The Safe Drinking Water Act (SDWA) was first passed by Congress under President Nixon in 1974. The purpose of the Safe Drinking Water Act was to protect public health by regulating the nation's public drinking water supply. The law was further amended in 1986 and 1996 and requires many actions to protect drinking water and its sources including rivers, lakes, reservoirs, springs, and ground water wells [USEPA, 2009].

The SDWA authorizes the EPA to set national health-based standards for drinking water. The standards are to protect against naturally-occurring and man-made contaminants that may be found in drinking water. For the standards to be met, the EPA, states, and water systems work together [USEPA, 2009].

Originally, the Safe Drinking Water Act focused primarily on treatment as the means of providing safe drinking water at the tap. However, the 1996 amendments greatly enhanced the existing law by recognizing source water protection, operator training, funding for water system improvements, and public information as important components of safe drinking water. This new approach ensured the quality of drinking water by protecting it from source to tap [USEPA, 2009].

2.2.1 Primary Standards

National Primary Drinking Water Regulations (NPDWRs or primary standards) are legally enforceable standards that apply to public water systems. Primary standards protect public health by limiting levels of contaminants in drinking water [USEPA, 2009].

There are six different categories for primary drinking water regulations: microorganisms, disinfectants, disinfection byproducts, inorganic chemicals, organic chemicals and radionuclides. Contaminants listed below pose documented health problems. Examples of microorganism contaminants are: Cryptosporidium, Giardia lamblia, Heterotrophic plate count, Legionella, turbidity, total coliforms and E. Coli and viruses. Examples of disinfectant contaminants are: chloramines, chlorine and chlorine dioxide. Examples of disinfection byproducts are bromate, chlorite, haloacetic acids and total trihalomethanes. Examples of inorganic chemicals are: arsenic, asbestos, barium, cadmium, chromium, copper, cyanide, lead, mercury, nitrate, nitrite, selenium and thallium. Examples of organic contaminants include: benzene, carbon tetrachloride, chlorobenzene, dioxin, ethylbenzene, polychlorinated biphenyls (PCBs), styrene, toluene, vinyl chloride and xylenes. Examples of radionuclide contaminants include: alpha particles, beta particles, radium, and uranium [USEPA, 2009].

2.2.2 Secondary Standards

National Secondary Drinking Water Regulations are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. The EPA recommends that water systems comply with secondary standards but does not require systems to comply. It is within the states' jurisdiction to choose to adopt them as enforceable standards. The 15 secondary drinking water regulations are as follows: aluminum, chloride, color, copper, corrosivity, fluoride, foaming agents, iron, manganese, odor, pH, silver, sulfate, total dissolved solids, and zinc [USEPA, 2009].

2.3 MANGANESE IN DRINKING WATER

With the current United States Environmental Protection Agency regulations on disinfection byproducts such as trihalomethanes and haloacetic acids, conventional methods of manganese removal may need to be reevaluated in treatment plants across America. Traditionally, across the United States, any combination of aeration, free chlorine, permanganate, sedimentation and filtration are used to remove manganese from drinking water.

Manganese in drinking water is a secondary contaminant established by the EPA. Secondary contaminants are not harmful to human health. Secondary contaminants are monitored for aesthetic reasons rather than health reasons. If there is more than 0.05 mg/L of manganese in the water, the water may have a "tea" color and will stain laundry and plumbing fixtures. A metallic taste and odor can accompany the undesirable water color.

Aeration can only be used for manganese treatment if there is room for a large aeration basin, since manganese oxidizes slowly when aerated. Oxidizing dissolved manganese with potassium permanganate is a delicate balancing act between insufficient dosing and overdosing of permanganate. Overdosing permanganate can also lead to discoloration of the finished water. Additionally, permanganate is pH dependent, so at low pH values, permanganate is actually reduced to the Mn^{2+} ion. If insufficient amounts of permanganate are added there will not be enough oxidant to oxidize manganese to manganese dioxide. If permanganate is overdosed then soluble manganese is passed through the filter and out to the distribution system.

The Pittsburgh Water and Sewer Authority drinking water plant uses potassium permanganate at the head of the treatment plant to oxidize the dissolved Mn^{2+} to solid manganese dioxide (MnO_2). Manganese dioxide is a black solid that can be settled or filtered.

Due to lower pH values in the coagulation/flocculation basins with enhanced coagulation, the potassium permanganate is actually being reduced to the Mn^{2+} ion.

There are two reactions that describe how permanganate reacts in acidic conditions. The first reaction is when the permanganate ion is reduced by the hydronium which loses a proton and forms water. The reduced permanganate forms the manganese ion which is not easily removable. The second reaction is when the permanganate ion is reduced by the hydronium ion, but only three electrons are transferred instead of five. The second reaction equation results in the desirable compound of manganese dioxide. The following are two reactions that occur in acidic conditions. The top equation will predominate [MWH, 2005].

$MnO_4^- + 8\ H_3O^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$ $\quad E°=1.51V \quad \Delta G= -728$ kJ/mole

$MnO_4^- + 4\ H_3O^+ + 3\ e^- \rightarrow MnO_2 + 2\ H_2O$ $\quad E°=1.68V \quad \Delta G= -486$ kJ/mole

The Gibbs Free Energy equation relates redox potential given by E°, Faraday's constant, the number of electrons transferred to Gibbs Free Energy. The reaction with the most negative Gibbs Free Energy will predominate. The following equation allows for the calculation of Gibbs Free Energy.

$$\Delta G = -nFE°$$

n=number of electrons (Number of moles of e^-)

F=Faraday's constant = 96,485 Coulomb/mole

E°=Reduction Oxidation Potential (Volts)

[MWH, 2005]

In alkaline solutions a similar reaction occurs. The potassium permanganate disassociates and becomes the permanganate ion. The permanganate ion oxididizes the Mn^{2+} ion and yields manganese dioxide. Manganese dioxide, the black powder, is easily removable with

multimedia filtration. In alkaline conditions, there is only one reaction that occurs. The Gibb's Free Energy for this reaction that yields manganese dioxide is more negative than the reaction that yields manganese dioxide in acidic conditions [MWH, 2005].

$$MnO_4^- + 2\ H_2O + 3\ e^- \rightarrow MnO_2 + 4\ OH^- \qquad E°=0.60V \qquad \Delta G= -174\ kJ/mole$$

In summary, if permanganate is used, alkaline conditions are necessary to attain manganese dioxide formation. In acidic conditions, the permanganate used will only add to the amount of dissolved manganese in the water.

Figure 4 is the manganese stability diagram that compares redox potential, pE, and pH. The figure shows what form of manganese is most prevalent given a certain pH and redox potential of the water.

At zero redox potential and in acidic conditions, pH -2 to 7, the manganese ion, Mn^{2+}, predominates among the different species of manganese. The permanganate ion, MnO_4^-, is present at elevated redox potential through all pH levels. The negatively sloping borders of manganese dioxide, MnO_2, explain how alkaline conditions are more favorable (lower redox potential) to yield manganese dioxide. As pH increases the redox potential drops to form manganese dioxide.

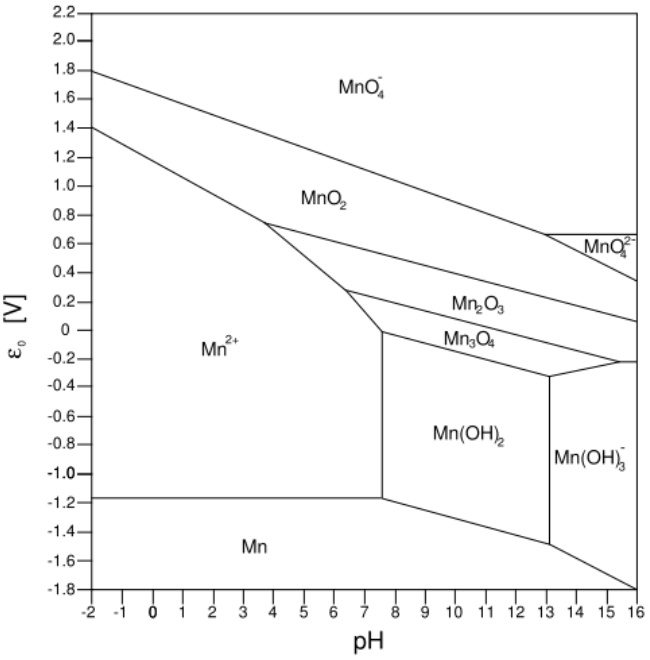

Figure 4. Manganese Pourbaix Diagram: pH versus Redox Potential of Manganese

[Rayner-Canham, 1996]

Manganese ion, Mn^{2+}, predominates through normal redox potential levels in drinking water in acidic conditions. Acid conditions here are defined by a pH less than 7.0. When the pH in drinking water is lowered to achieve enhanced coagulation, Mn^{2+} predominates. Either an oxidizing agent such as permanganate or free chlorine needs to be added, to increase the redox potential, or the pH needs to be increased to yield manganese dioxide. Manganese dioxide is the ideal speciation of manganese for removal since it is a solid and can be removed by sedimentation and filtration. The above reasoning supports why enhanced coagulation without the addition of an oxidizing agent (chlorine) hinders manganese removal.

Due to aeration's large footprint requirements and permanganate's pH dependence and operational difficulties, free chlorine is often used to oxidize manganese. Low amounts (0.3 -0.6 mg/L) of free chlorine are used to oxidize manganese to manganese dioxide which is then removed by multimedia filters. Free chlorine is used to oxidize manganese because it is not as

pH sensitive as permanganate treatments. If an operator were to overdose the prefilter chlorine, the manganese levels would not increase the same way potassium permanganate makes the manganese levels rise in the presence of an overdose. On the other hand if sodium hypochlorite is overdosed the concentrations of THMs increase which is more of a health hazard than "tea colored" water from the manganese.

2.4 DISINFECTION AND DISINFECTION BYPRODUCTS

Disinfectants are used to control many different microorganisms that are found in drinking water. Chlorine, a standard disinfectant reacts with naturally occurring organic and inorganic matter in source water and distribution systems to form disinfection byproducts (DBP). Results from toxicology studies have shown several disinfection byproducts to be carcinogenic in laboratory animals. Some of these DBPs include chloroform, dichloroacetic acid, bromodichloromethane, bromoform, and bromate. Other disinfection byproducts such as bromodichloromethane, chlorite, and certain haloacetic acids have shown to cause adverse reproductive and or developmental effects in laboratory test animals. Recent surveys show that more than 200 million people in the United States consume water that has been disinfected. Because of the large population exposed, health risks associated with DBPs, even if small, need to be controlled using appropriate measures [USEPA, 2006].

The purpose of the Environmental Protection Agency's Stage 2 Disinfectants and Disinfection Byproducts Rule is to increase public health protection by reducing the potential risk of adverse health effects associated with disinfection byproducts throughout the distribution system. This rule builds on the Stage 1 Disinfectants and Disinfection Byproducts Rule by

focusing on monitoring and reducing concentrations of the two classes of DBPs Total Trihalomethanes and five haloacetic acids [USEPA, 2007].

In order to comply with the new disinfection byproduct regulation, PWSA followed EPA recommendations and instituted enhanced coagulation. Enhanced coagulation is when the coagulation process occurs at a lower pH value (usually less than 6.8) and a grater dose of coagulant is added during the rapid mix unit process. Studies have shown that when sweepfloc occurs at lower pH values the natural organic matter will adhere to the floc particles. If the pH is higher, the organic matter will not as effectively attach to the particles. Because Pittsburgh uses enhanced coagulation, it is necessary to re-oxidize the manganese before the filter because of the low pH value. It is important to remove organic carbon because organic carbon is a precursor for trihalomethanes and haloacetic acids. The figure below shows the correlation between Total Organic Carbon (TOC) and THM formation.

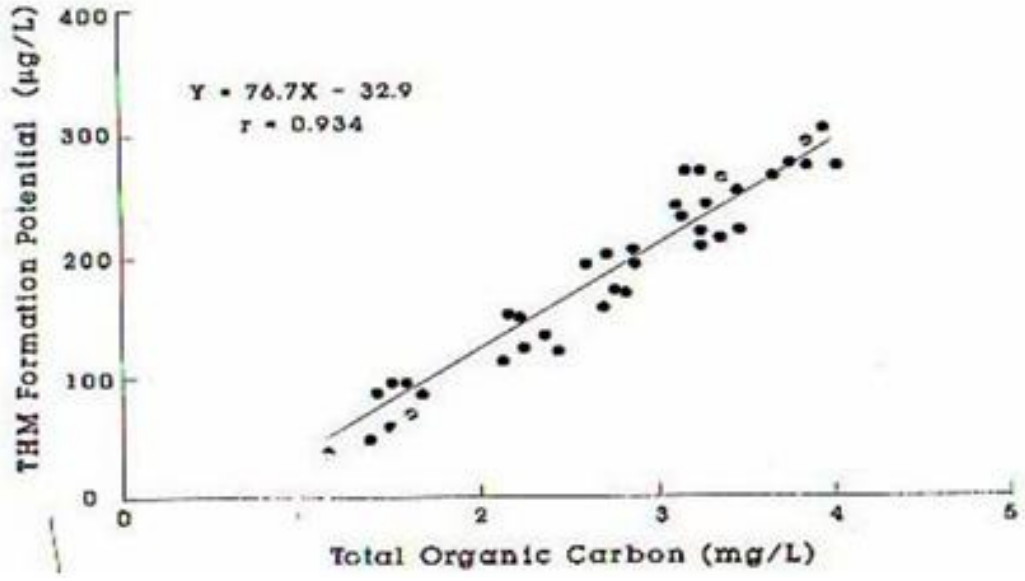

Figure 5. Effects of TOC on THM Formation Potential
[Bitton, 2005]

Total organic carbon between the levels of 1 and 4 mg/L show a direct correlation with trihalomethane formation on the scale of 100-300 μg/L. The r^2 value for this data set is 0.872 which indicates a linear relationship is present. TOC is used as an indicator for THM formation potential. One of the reasons for using TOC as an indicator is the TOC test takes one hour and the THM formation potential analysis takes at least five days.

Trihalomethane formation is strongly dependent on the chlorine concentration in the water. However, in the literature there is some disagreement regarding the quantitative relationship between the chlorine concentration and the rate of THM production. Most investigators of this have found a linear relationship between chlorine consumption and the production of THMs with the reaction order greater or equal to one [Kavanough M. C., 1980].

Efforts are made in water treatment to control the concentration of trihalomethanes, however research suggests that the distribution of chlorinated water can more than 120% of the trihalomethanes formed in the treatment plant. This may be caused by the low velocity in the pipelines or the high residence time in reservoirs [El-Shafy &Grunwald, 2000].

In order to oxidize the manganese, free chlorine is used because even at low pH values $Mn^{2+} \rightarrow MnO_2$. Now that the plant water is at a lower pH, manganese is reduced again to its dissolved ionic state. Multimedia filters do not remove ions, the can only remove solid particles. THMs and HAAs are formed by chlorine oxidizing organic matter to create carcinogenic byproducts. The chlorine will either oxidize the organic matter or replace hydrogen to make chlorinated organic compounds. There is a delicate balance of adding enough chlorine to oxidize the manganese but not to drastically increase the amount of THMs produced. The Pittsburgh Water and Sewer Authority is exploring any means to reduce chlorine usage, contact time and the reduction of total organic carbon to limit DBP formation. The dose of chlorine varies in

PWSA because of changing manganese loading. The prefilter chlorination dose is usually within the range of 0.30 to 0.45 mg/L. The following is the equation that shows how free chlorine interacts with manganese in solution:

$$Mn^{2+} + HOCl + H_20 \rightarrow MnO_2 + Cl^- + 3H^+$$

Free chlorine takes the form of hypochlorous acid (HOCl) or hypochlorite ion (OCl^-) depending on the pH level of the water. Free chlorine oxidizes the manganese ion which yields manganese dioxide. The remaining products are a chloride ion which has no effect on the drinking water and three protons which lowers the pH level.

An additional problem with using chlorine to oxidize manganese is that the chlorine is being added before the filter to settled water. Filters remove organic material therefore creating less DBPs in the clearwell when chlorine is added. When prefilter chlorination occurs, water with elevated organic carbon concentration is dosed with chlorine.

Natural organic matter (NOM) contains many rings and functional groups. The free chlorine will attack and replace certain hydrogen molecules. If these newly chlorinated functional groups break their bonds to the NOM, small chlorinated organics are formed such as haloacetic acids and trihalomethanes. Haloacetic acids and trihalomethanes are regulated by EPA's Stage 2 Disinfectants and Disinfection Byproducts Rule.

The possibility of using permanganate right before the filter would be a viable option to re-oxidize the dissolved manganese. The problem with using permanganate to oxidize manganese is manganese is being removed with manganese and if the operator overdoses the permanganate, then the operator will pass manganese to the finished water.

A novel approach in this research is using hydrogen peroxide to oxidize manganese. Hydrogen peroxide is a stronger oxidant than free chlorine and it does not create any of the

halogenated byproducts subject to regulation by Stage 2 DBP Regulation. Hydrogen peroxide is a very strong oxidant and has disinfection properties as well. One unknown in the research thus far is that the peroxide might oxidize the organics and there is no research on whether or not the resulting molecule is carcinogenic or harmful in other ways. The following is the mechanism that shows how peroxide oxidizes dissolved manganese:

$$Mn^{2+}_{(aq)} + H_2O_2 \rightarrow MnO_{2(s)} + 2\ H^+$$

The redox equation above is solved by the combination of a reduction equation and an oxidation equation. Below is the oxidation equation:

$$Mn^{2+}_{(aq)} + 2\ H_2O \rightarrow MnO_{2(s)} + 4\ H^+ + 2\ e^-$$

Manganese is oxidized by two water molecules and yields manganese dioxide along with four protons and two electrons. In the reduction reaction, hydrogen peroxide is reduced by two protons and with the exchange of two electrons, two water molecules are formed. When combining the oxidation and the reduction equations, the electrons cancel and the water molecules cancel and all but two protons cancel.

The reduction equation follows:

$$H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O$$

After the combination the final equation looks like this:

$$Mn^{2+}_{(aq)} + H_2O_2 \rightarrow MnO_{2(s)} + 2\ H^+$$

Protons are in both the reduction and oxidation reaction, therefore pH affects the product yield. If the water is acidic the equation will go towards the left because of the common ion effect. So, here again it is important to increase the pH after the enhanced coagulation step to ensure the reaction proceeds favorably.

Throughout this research, the only disinfection byproduct that was tested for and analyzed was total trihalomethanes. The reason for this is that PWSA has never come close to violation of the EPA's Stage 2 Disinfectants and Disinfection Byproducts Rule because of haloacetic acids and therefore did not wish to focus the research on haloacetic acids. Total trihalomethanes formation correlates with haloacetic acid formation and hypotheses can be made about the effectiveness of the different methods for the minimization of all disinfection byproducts.

2.4.1 Stage 1 Regulations of Disinfection Byproducts

In the past, the Safe Drinking Water Act (SDWA) has been highly effective in protecting public health and has also evolved to respond to new and emerging threats to safe drinking water. Arguably, disinfection of drinking water was one of the major public health advances in the 20th century. One hundred years ago, typhoid and cholera epidemics were common through American cities and disinfection was a major factor in reducing these epidemics [USEPA, 2006].

However, the disinfectants used in drinking water can react with naturally-occurring materials in the water to form unintentional byproducts which may pose health risks. Also, in the past ten years, the scientific community has learned that there are specific microbial pathogens, such as Cryptosporidium, which can cause illness and is resistant to traditional disinfection practices due to its ability to form an oocyst [USEPA, 2006].

Amendments to the Safe Drinking Water Act in 1996 required the EPA to develop rules balancing the risks between microbial pathogens and disinfection byproducts. It is important to strengthen protection against microbial contaminants, especially Cryptosporidium, and at the same time, reduce potential health risks of DBPs. The paradox of disinfection requires greater

removal of chlorine resistant microorganisms without using more chlorine. The Stage 1 Disinfectants and Disinfection Byproducts Rule and Interim Enhanced Surface Water Treatment Rule, announced in December 1998, are the first of a set of rules under the 1996 SDWA Amendments [USEPA, 2006].

While disinfectants are effective in controlling many microorganisms, they may react with natural organic and inorganic matter in source water and distribution systems to form DBPs. Results from toxicology studies have shown several DBPs (e.g., bromodichloromethane, bromoform, chloroform, dichloroacetic acid, and bromate) to be carcinogenic in laboratory animals. Other DBPs (e.g., chlorite, bromodichloromethane, and certain haloacetic acids) have also been shown to cause adverse reproductive and or developmental effects in laboratory animals. There have been several epidemiology studies that have suggested a weak association between certain cancers (e.g., bladder) or reproductive and developmental effects, and exposure to chlorinated surface water. In the United States, more than 200 million people consume water that has been disinfected. Because of the large population exposed, health risks associated with DBPs, even if small, need to be taken seriously [USEPA, 2006].

The Disinfectants and Disinfection Byproduct Rule establishes maximum residual disinfectant level goals (MRDLGs) and maximum residual disinfectant levels (MRDLs) for three chemical disinfectants - chlorine, chloramine and chlorine dioxide (see Figure 6). The rule also establishes maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for total trihalomethanes, haloacetic acids, chlorite and bromated methanes shown in Figure 6 [USEPA, 2006].

DISINFECTANT RESIDUAL	MRDLG (mg/L)	MRDL (mg/L)	COMPLIANCE BASED ON
Chlorine	4 (as Cl_2)	4.0 (as Cl_2)	Annual Average
Chloramine	4 (as Cl_2)	4.0 (as Cl_2)	Annual Average
Chlorine Dioxide	0.8 (as ClO_2)	0.8 (as ClO_2)	Daily Samples
DISINFECTION BYPRODUCTS	MCLG (mg/L)	MCL (mg/L)	COMPLIANCE BASED ON
Total trihalomethanes (TTHM)[1] - Chloroform - Bromodichloromethane - Dibromochloromethane - Bromoform	N/A *** 0 0.06 0	0.080	Annual Average
Haloacetic acids (five) (HAA5)[2] - Dichloroacetic acid - Trichloroacetic acid	N/A 0 0.3	0.060	Annual Average
Chlorite	0.8	1.0	Monthly Average
Bromate	0	0.010	Annual Average

Figure 6. MRDLGs, MRDLs, MCLGs and MCLs for Stage 1 Disinfectants and Disinfection Byproducts Rule

2.4.2 Stage 2 Regulations of Disinfection Byproducts

The Stage 2 DBP rule is one part of the Microbial and Disinfection Byproducts Rules (MDBPs), which are a set of interrelated regulations that address risks from microbial pathogens and disinfectants and disinfection byproducts. The Stage 2 DBP rule focuses on public health protection by limiting exposure to DBPs, specifically total trihalomethanes and five haloacetic acids. Trihalomethanes and haloacetic acids can form in water that has been disinfected to control microbial pathogens [USEPA, 2007].

The Stage 2 Disinfection Byproducts Rule will reduce potential cancer and reproductive and developmental health risks from disinfection byproducts in drinking water, which form when disinfectants are used to control microbial pathogens [USEPA, 2007]. These reductions expand upon the Stage 1 Disinfection Byproducts Rule discussed in the previous section.

This final rule strengthens public health protection for customers by tightening compliance monitoring requirements for two groups of DBPs, trihalomethanes and haloacetic acids. The rule targets systems with the greatest risk and builds incrementally on existing rules [USEPA, 2007].

Under the Stage 2 DBPR, systems will conduct an evaluation of their distribution systems, known as an Initial Distribution System Evaluation (IDSE). The purpose of the IDSE is to identify the locations with high disinfection byproduct concentrations. The locations identified will then be used by the systems as the sampling sites for Stage 2 DBPR compliance monitoring [USEPA, 2007].

In compliance with the Stage 2 DBPR, the maximum contaminant levels for two groups of disinfection byproducts are calculated for each monitoring location in the distribution system. This approach, referred to as the locational running annual average (LRAA), differs from previous requirements, which determined compliance by calculating the running annual average of samples from all monitoring locations across the system [USEPA, 2007].

2.4.3 Disinfection Byproduct Precursors

Total organic carbon (TOC) is an important indicator of water quality in drinking water supply systems. Prescribed chlorination rates are often based on TOC levels, and levels of disinfection byproducts (DBP) can be subsequently approximated. Note Figure 5 in section 2.4 for the correlation between TOC and THM formation. Unfortunately, TOC is time consuming to measure, and some water utilities rely on the more easily measured absorbance of ultraviolet light (specifically at a wavelength of 254 nm) as a surrogate indicator of organic content [Westphal, Chapra, & Sung, 2004].

Both TOC and UV 254 absorbance measure organic matter in water. The concentration of organic matter in water correlates with the concentration of disinfection byproducts after chlorination. UV 254 absorbance can provide inexpensive and meaningful prescriptive guidance for disinfection processes especially for daily operating purposes. A more accurate and accepted portrayal of organic matter concentration is achieved by measuring total organic carbon. UV 254 absorbance can be used in addition to TOC testing to provide additional data on organic matter concentration and removal.

A study by Westphal, Chapra, and Sung showed that TOC and UV 254 absorbance are correlated reasonably well in a water supply reservoir for Boston, MA, and that a simple mass balance tool can effectively assist with planning and operations management using UV 254 absorbance as a primary water quality indicator [Westphal, Chapra, & Sung, 2004].

2.4.3.1 TOC and UV 254 Absorbance

In comparing mg/L of total organic carbon and absorbance retained from a light source at 254 nanometers, oftentimes the numbers will not directly coincide. However there is a correlation. In the Westphal study, UV 254 absorbance and TOC data was collected in accordance to standard methods on weekly and monthly intervals from 1997 through 2001. The weekly values were averaged into monthly values to minimize the impact of isolated scatter and measurement noise, thereby better capturing the overall trend in the correlation. Monthly values from throughout the system are plotted in figure 7 and monthly values from only the Cosgrove Intake are plotted in figure 8. Figures 7 and 8 reveal that TOC and UV 254 absorbance appear to be well correlated regardless of sampling location and regardless of residence time [Westphal, Chapra, & Sung, 2004].

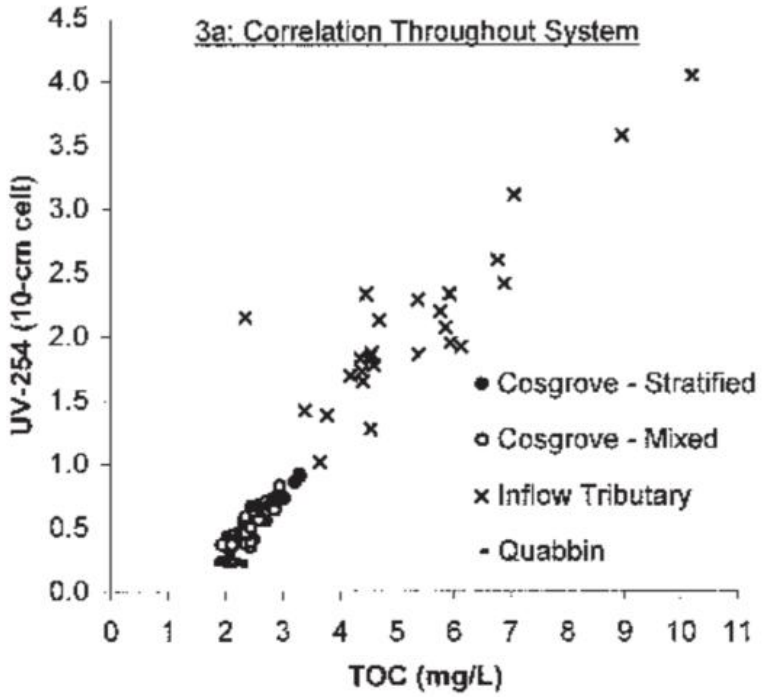

Figure 7. Correlation of TOC and UV 254 Absorbance for Whole System in Westphal Study

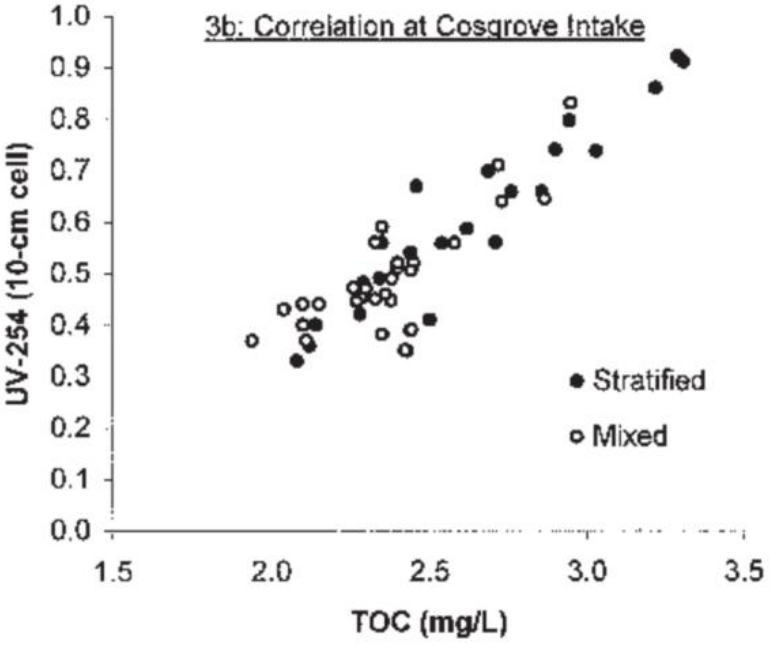

Figure 8. Correlation of TOC and UV 254 Absorbance for Cosgrove Intake in Westphal Study

Westphal used an ordinary least squared linear regression and obtained the following R^2 values: for the correlation though out the system, $R^2 = 0.91$ and for the correlation at the

Cosgrove Intake, $R^2 = 0.81$ [Westphal, Chapra, & Sung, 2004]. The Westphal study concludes that TOC and UV 254 absorbance are related and are well correlated. The correlation explains similar trends in organic matter reduction above and below the filters in pilot and plant studies completed at PWSA.

If funding or access to a TOC instrument is a problem, UV 254 absorbance can serve as an adequate substitute to TOC testing. Total organic carbon testing is still the best disinfection byproduct precursor but UV 254 absorbance is acceptable.

2.5 HYDROGEN PEROXIDE AND WATER TREATMENT

Hydrogen Peroxide is one of the most powerful oxidizers known in water treatment, stronger than chlorine, chlorine dioxide, and potassium permanganate. Through catalysis, H_2O_2 can be converted into hydroxyl radicals ($^{\bullet}OH$) with reactivity second only to fluorine. Below is a table that ranks oxidation potential of seven strong oxidants. Hydrogen peroxide ranks just under ozone and 0.4 Volts stronger than free chlorine [U.S. Peroxide, 2005].

Table 1. Oxidation Potential of 7 Strong Oxidants

Oxidant	Oxidation Potential (Volts)
Fluorine	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Chlorine dioxide	1.5
Chlorine	1.4

Despite its power, hydrogen peroxide is a natural metabolite of many organisms, which decompose the H_2O_2 they produce into oxygen and water. H_2O_2 is also formed by the action of sunlight on water, a natural purification system for our environment. Consequently, H_2O_2 has none of the problems of gaseous release or chemical residues that are associated with other chemical oxidants. And since hydrogen peroxide is totally soluble with water, the issue of safety is one of concentration. Industrial strength H_2O_2 is a strong oxidizer and as such requires special handling precautions [U.S. Peroxide, 2005].

The fact that H_2O_2 is used for seemingly converse applications proves its versatility. For example, hydrogen peroxide can inhibit microbial growth (as in the bio-fouling of water circuits) and encourage microbial growth (as in the bioremediation of contaminated ground waters and soils). Similarly, it can treat both easy-to-oxidize pollutants (iron and sulfides) and difficult to oxidize pollutants (solvents, gasoline and pesticides) [U.S. Peroxide, 2005]. Hydrogen peroxide's oxidation potential and its lack of byproducts served as selling points to H_2O_2 as a manganese oxidant for municipal drinking water treatment.

2.5.1 Hydrogen Peroxide and Chlorine Interaction

An unforeseen phenomenon occurred during the bench-scale experiment described in section 3.1. A reaction between hydrogen peroxide and the free chlorine occurred. The reaction between hydrogen peroxide chlorine in hydrochloric acid solutions proceeds according the equation:

$$Cl_2 + H_2O_2 \rightarrow O_2 + 2H^+ + 2Cl^-$$

The rate of this reaction has been studied by Makower and Bray [1933]. In hydrochloric acid solutions of greater than one molal concentration Makower and Bray found that the rate law to be [Connick, 1947]:

$$-\frac{d(H2O2)}{dt} = -\frac{d(Cl2)}{dt} = k\frac{(H2O2)(Cl2)}{(H+)(Cl-)}$$

Makower and Bray accounted for this equation by assuming the chlorine was in rapid equilibrium with its hydrolysis products and that the rate determining step was the reaction between hydrogen peroxide and hypochlorous acid [Connick, 1947]:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

$$HOCl + H_2O_2 \rightarrow H_2O + O_2 + H^+ + Cl^-$$

Hydrogen peroxide and free chlorine are both strong oxidants. In the reduction oxidation tables, shown in Table 1, hydrogen peroxide is a stronger oxidant. In the above reaction, the free chlorine is being oxidized to a chloride ion and the hydrogen peroxide is being reduced to water and oxygen.

Using hydrogen peroxide to oxidize manganese and shortly thereafter disinfecting the water with chlorine created new problems. Since the hydrogen peroxide oxidizes the free chlorine and the chemical reaction yields the chloride ion, useless in disinfection, it is not feasible to use hydrogen peroxide so close to chlorine in the treatment process. In PWSA's drinking water plant there is an 8 hour time before the post filter water flows into the clear well. The clear well is where the chlorine is added for disinfection.

The half life of hydrogen peroxide ranges from 8 hours to 20 days depending on the microbiological activity and metal contamination of the water [FMC Corporation, 2008]. So even if the hydrogen peroxide is added at the head of the treatment works, PWSA's detention

time of 3 days is not long enough for the hydrogen peroxide to dissipate and allow the chlorine to disinfect uninhibited.

2.6 PERMANGANATE AND WATER TREATMENT

Potassium Permanganate ($KMnO_4$) is commonly used to oxidize both iron and manganese. Potassium permanganate can also be used in regenerating a manganese greensand filter bed. Permanganate is a purple crystal and is sold 95 to 99% pure depending on the supplier. Permanganate reacts vigorously with organic materials such as powder activated carbon, oil and greases. Extreme care and caution must be used when handling, storing, and dosing potassium permanganate. Reactions with other chemicals can result in violent spontaneous explosions. $KMnO_4$ should be stored in a cool dry place, humidity and moisture causes caking of the $KMnO_4$ crystals [Sommerfeld, 1999].

The rate of manganese oxidation from dosing potassium permanganate is influenced by both pH and temperature. Manganese oxidation at pH values between 5.5 and 9.0 generally occurs within ten seconds at a temperature of 25° C. At a temperature of 2° C the oxidation could take longer than two minutes. Increasing the pH, usually with soda ash, increases manganese oxidation kinetics [Sommerfeld, 1999].

2.7 COAGULANT OPTIONS

In the United States, the predominant water treatment coagulant is aluminum sulfate, or "alum," because it is a very effective chemical and has a low cost. When ferric or aluminum ions are added to water, a number of reactions occur. When a salt of aluminum, Al(III), and iron, Fe(III), is added to water, it will dissociate to yield trivalent Al^{3+} and Fe^{3+} ions, as given below [MWH, 2005]:

$$Al_2(SO_4)_3 \leftrightarrow 2\ Al^{3+} + 3SO_4^{2-}$$

$$FeCl_3 \leftrightarrow Fe^{3+} + 3Cl^-$$

The resultant trivalent metal neutralizes the negatively charged particles in the raw water and begins to form flocculent particles. The solubility of trivalent aluminum and iron ions is dependent on concentration of coagulant and the pH of the receiving water. Solubility diagrams portray the relationship between coagulant dose, speciation of the metal and pH level [MWH, 2005].

If an excessive amount of metal coagulant is used, sweep floc occurs. Sweep floc occurs when the dose of a coagulant is increased so much that solubility is exceeded. When sweep floc is attained particles gravity settle in a reasonable amount of time for water treatment [MWH, 2005].

2.7.1 Aluminum Sulfate

Aluminum sulfate is the United States most popular coagulant, mostly because it is highly effective and its low cost. Alum has greater pH limitations with respect to solubility than its ferric counterparts. Figure 9 shows that the operating region for aluminum hydroxide

precipitation is in a pH range of 5.5 to 7.7, with minimum solubility occurring at a pH of about 6.2 at 25 °C. The typical operating rage for aluminum sulfate is indicated by the shaded box in figure 9 [MWH, 2005].

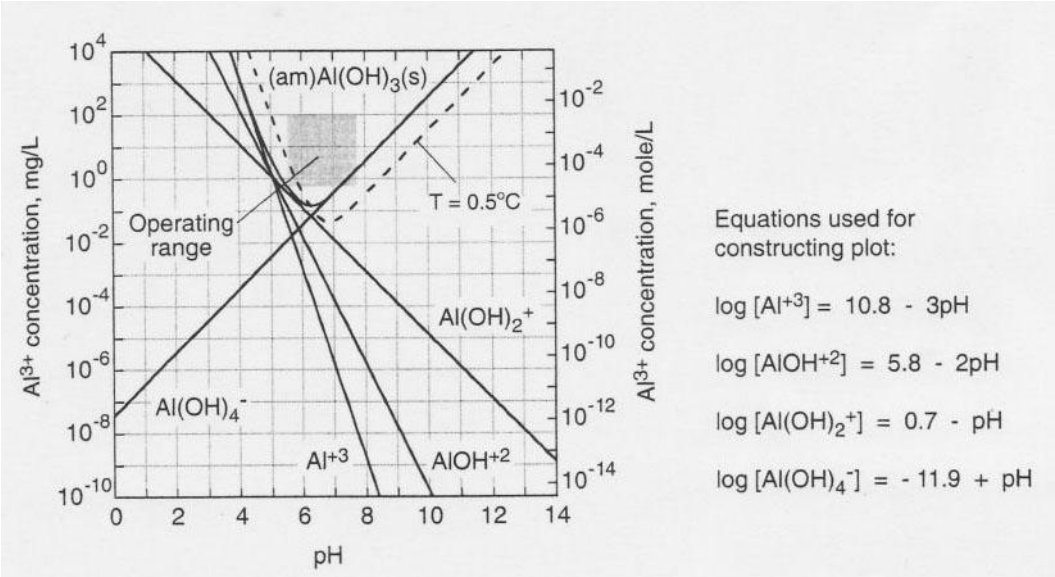

Figure 9. Solubility Diagram for Aluminum Sulfate: Al(III)
[MWH, 2005]

Studies suggest that Alzheimer's disease may be more prevalent in waters treated with alum due to higher aluminum concentrations found in the drinking water [Alzheimer's Society, 2008]. Thus, PWSA does not use alum as a coagulant.

2.7.2 Ferric Sulfate

Ferric chloride and ferric sulfate are similar coagulant. Both ferric chloride and ferric sulfate have the same coagulation processes and effectiveness. However, the major difference between the two is price and manganese contamination. Ferric chloride is known in the water treatment industry to be contaminated with manganese. At PWSA, the manganese levels are often higher in the flume then in the raw water. The increase in manganese concentration is partly due to

potassium permanganate added, but additional jar tests performed by PWSA concluded an increase of manganese after the ferric chloride was added. The downside to ferric sulfate is the price. It is more expensive than ferric chloride and aluminum sulfate [States, 2009].

Figure 10 below shows that the operating region for iron hydroxide precipitation is in a pH range of 5.0 to 8.5, with minimum solubility occurring at a pH of about 8.0 at 25 °C. The ferric coagulants are more insoluble than the aluminum coagulants over a wider pH range. The ability to not dissolve (remain insoluble) makes ferric coagulants a better choice in charge destabilization. The typical operating rage for ferric sulfate and ferric chloride is indicated by the shaded box in figure 10 [MWH, 2005].

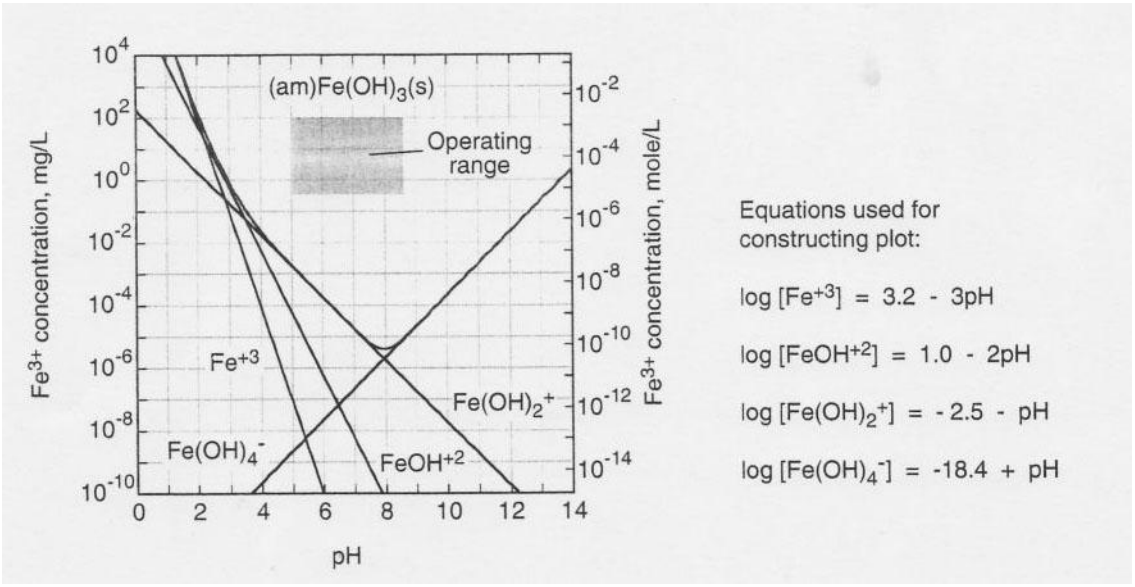

Figure 10. Solubility Diagram for Ferric Sulfate and Ferric Chloride: Fe(III) [MWH, 2005]

2.7.3 Ferric Chloride

The Pittsburgh Water and Sewer Authority uses ferric chloride as a coagulant in its water treatment plant. PWSA originally used alum due to cost and effectiveness, but when a speculation of Alzheimer's disease is caused by the ingestion of aluminum, the utility switched

to ferric chloride. PWSA has historically had high iron and manganese in its raw water. The elevated levels of iron manganese stem from the years of steel production, coal mining and acid mine drainage. PWSA has made great efforts to remove manganese without increasing disinfection byproduct levels (adding additional chlorine). Experiments were designed to look into the effectiveness of both ferric chloride and ferric sulfate with respect to iron and manganese concentration, turbidity, TOC, and UV 254 absorbance.

Figure 10 above shows that the operating region for iron hydroxide precipitation is in a pH range of 5.0 to 8.5, with minimum solubility occurring at a pH of about 8.0 at 25 °C. Comparing the solubility of alum and ferric species, the ferric species are more insoluble than aluminum species and are also insoluble over a wider pH range. The ability not to dissolve makes the ferric ion the coagulant of choice to aid in charge destabilization

3.0 BENCH-SCALE EXPERIMENTS

Preliminary experiments were performed to measure concentrations of trihalomethanes (THMs), manganese, iron, total organic carbon (TOC), UV 254 absorbance, and chlorine in PWSA's drinking water. The purpose of the bench-scale experiments was to test a multitude of hypotheses while easily altering the testing parameters. The majority of the preliminary bench-scale experiments were jar tests.

Jar testing is a method of simulating a full-scale water treatment process to provide system operators a reasonable idea of the way a treatment chemical will behave and operate with a particular type of raw water. Because it mimics full-scale operation, system operators can use jar testing to help determine which treatment chemical will work best with their system's raw water [Satterfield, 2005].

The first experiment of the research investigated using hydrogen peroxide as an oxidant for iron and manganese in drinking water. The hydrogen peroxide was dosed prefilter and the oxidized metals were removed on the filter. Hydrogen peroxide was used as an alternative to free chlorine, which is currently used in most drinking water plants with iron and manganese issues.

Oxidation reduction reactions are pH dependent. The greater the pH, the more favorable it is for an oxidant to oxidize a metal. In a follow up jar test, hydrogen peroxide was reexamined at elevated pH levels and elevated doses.

In an effort to remove manganese, special attention was paid to treatment chemicals with high levels of manganese contamination. PWSA uses ferric chloride as a coagulant and ferric chloride is notorious for manganese contamination. Often times the water in the flume has higher manganese concentrations than the raw river water. A series of jar tests were devised to test ferric chloride and ferric sulfate as alternative coagulants. The reasoning behind the test was that both ferric chloride and ferric sulfate are trivalent iron coagulants and should be equally effective. However, ferric chloride contains more manganese than ferric sulfate. If ferric sulfate is used, there will be less additional manganese added with ferric sulfate, which means less manganese that needs removed on the filters. The question that needed answering was with all other parameters being equal, does an alternative coagulant with historically less manganese contamination make a significant impact on manganese removal in PWSA's drinking water.

PWSA already incorporates permanganate oxidation for manganese removal in the treatment plant; however the potassium permanganate is dosed at the head works of the plant. Enhanced coagulation drops the pH level and greatly reduces the effectiveness of permanganate's oxidation potential. The next jar test explored the possibility of dosing permanganate directly above the filters in addition to the rapid mix unit process of PWSA's treatment plant. The major drawback of using free chlorine to oxidize iron and manganese is the disinfection byproducts. Permanganate oxidation does not have carcinogenic repercussions. The sodium permanganate bench scale experiment was scaled up to a pilot-scale experiment and is discussed in detail in following sections.

Similarly to the hydrogen peroxide jar tests at elevated pH values, two additional jar tests were used to observe the effects of lower doses of prefilter chlorine and lower doses of sodium

permanganate dosed above the filters at elevated pH levels. The hypothesis was to lower the oxidizing chemical dose by increasing the pH level.

In addition to the jar tests and subsequent pilot studies, full plant-scale experiments were also used to aid in understanding plant optimization. A major question of the research was how prefilter chlorination affects the overall trihalomethane formation potential. This question was addressed by two types of experiments, the first being a prefilter chlorination plant study and the second being a chlorine spike study. Both experiments were designed to determine whether prefilter chlorination is a substantial contributor in THM formation. The following sections detail the experiments introduced above.

3.1 CHLORINE AND HYDROGEN PEROXIDE JAR TESTS

The chlorine and hydrogen peroxide experiment was devised to test a few hypotheses, namely does hydrogen peroxide effectively oxidize iron and manganese, does hydrogen peroxide reduce the amount of trihalomethanes formed and is hydrogen peroxide oxidation a viable alternative to prefilter chlorination. A bench-scale experiment involving the reaction of hydrogen peroxide and free chlorine was set up to test these hypotheses. If effective, hydrogen peroxide will be used before the filter in the PWSA treatment plant order to oxidize the manganese in the water. The effects of hydrogen peroxide pretreatment on TOC were also examined in this experiment.

This set of experiments tests for any unforeseen chemical reaction between the hydrogen peroxide used to oxidize manganese and the free chlorine used for disinfection.

3.1.1 Materials and Methods

1. Twenty-four hours prior testing, 6 Liters of flume water was collected and settled in 1 Liter Imhoff cones for 24 hours. The 24-hours of settling ensures that the samples taken the next day from the top of the filter are from the same "pocket" of water as the water on top of the filters in PWSA's treatment plant.
2. Two Liters of water were taken from the top of the filter on the day of the testing. The filter that was chosen was backwashed the previous evening. The prefilter chlorine was still being dosed at PWSA's treatment plant.
3. On the day of the experiment, the bottom of the Imhoff cone was removed and the sediment drained to waste. Exactly 1 Liter of water remained in the Imhoff cone.
4. There were 6 - 1 Liter beakers filled and placed on the gang stirrer. A description of the six beakers is as follows:

Table 2. Hydrogen Peroxide and Chlorine Jar Test Setup: 31 October 2008

	Jar 1	**Jar 2**	**Jar 3**	**Jar 4**	**Jar 5**	**Jar 6**
Sampled From	Flume	Flume	Flume	Flume	Top of Filter	Top of Filter
Hydrogen Peroxide	No	No	Yes	Yes	No	No
Prefilter Chlorine	No	No	No	No	Yes	Yes

The first jar of the experiment contained flume water settled for 24 hours. The second jar also contained flume water settled in an Imhoff cone for 24 hours. Jar number 3 contained settled flume water with 3 mg/L of hydrogen peroxide. Jar 4 also contained settled flume water with 3 mg/L of hydrogen peroxide. The fifth jar contained water collected on the day of the experiment from the top of the filter. The jar contained prefilter chlorinated water. Jar number 6 contained water collected on the day of the experiment from the top of the filter. The jar

contained prefilter chlorinated water. Figure 11 below shows an example of gang stirrer used for bench-scale and jar tests.

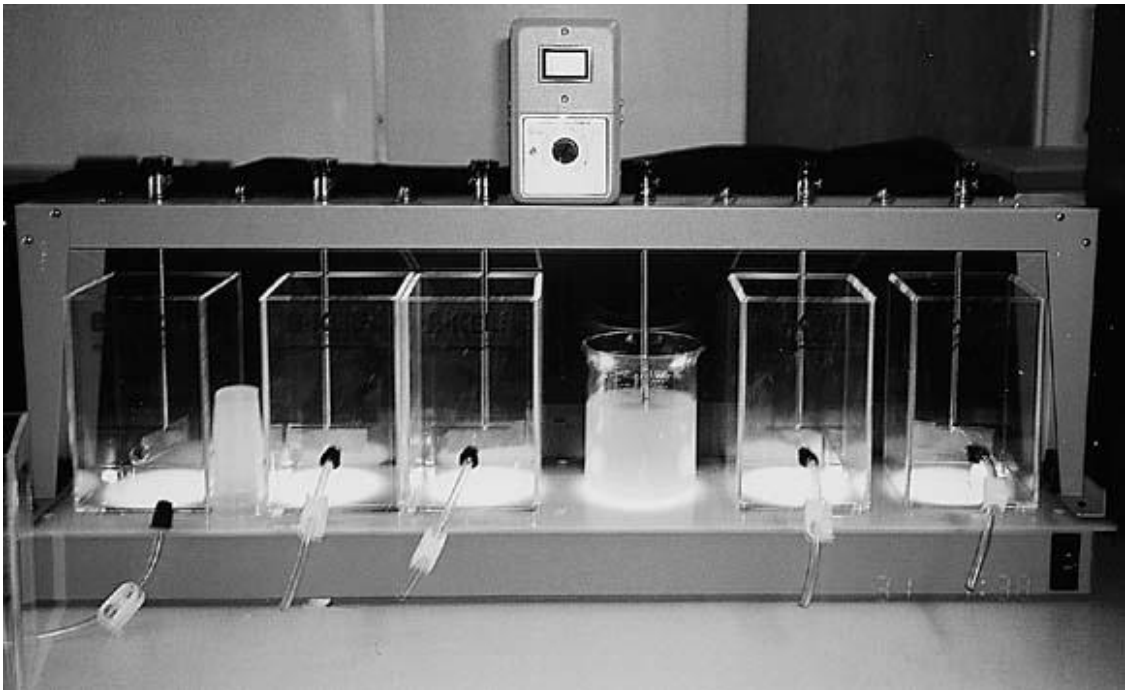

Figure 11. Gang Stirrer Used for Jar Tests
[Nguyen-Tang, 2002]

5. The first step was to dilute 3% store bought hydrogen peroxide to 3 mg/L hydrogen peroxide by taking a 10% dilution of H_2O_2 in a separate container (i.e. 10 mL of 3% peroxide into 100 mL solution) and then pipetting 1 mL of this working solution into a 1 L jar test to achieve 3 mg/L of 100% H_2O_2.
6. Next, the mixer on all six beakers was operated at 15 RPM for 10 minutes and then add 3 mg/L of hydrogen peroxide to beakers 3 and 4. The 15 RPM mixing replicated the gentle mixing in the flocculation basin.
7. Finally, the 6 beakers had no mixing for 50 minutes for quiescent settling.
8. A sample each beaker of was run on the Atomic Absorption instrument (AA) for iron and manganese.

a. The testing tube for the AA was pre-rinsed in Milli-Q® ultrapure water. The next step was to submerge each tube in one to one nitric acid and then Milli-Q® ultrapure water was used to rinse off the acid. The tubes were handled with plastic forceps so no additional metal contamination took place.
b. 100 mL of Milli-Q® ultrapure water was put through the 0.45 micrometer filter to ensure there is no residue on the filter before the run.
c. The dissolved and total levels for iron and manganese were recorded.

9. The set up of the 0.45 micrometer filter that was used for the AA sampling was used to simulate filtration for the jar test. The filtered sample was collected in a flask. This water was used in the following steps of the procedure.
10. The plant sodium hypochlorite solution is between 10-14% concentration. 1.10 mL of the concentrated hypochlorite solution was pipetted and diluted into 1 Liter of deionized (DI) water. A 100 mg/L chlorine working solution was created. Then, 10 mL of this working solution was pipetted into the 1 Liter jar test sample that was previously filtered. The handheld HACH chlorine meter was checked to ensure the reading of free chlorine. The chlorine was calculated to be 1 mg/L plus or minus 0.1 mg/L.
11. A smaller dosage of hypochlorite was added to jars 5 and 6. The smaller dosage is due to the jars already having been prefilter chlorinated. The final concentration of the all of the jars was 1 mg/L of chlorine. The final concentrations of each jar were verified by the handheld HACH chlorine meter.
12. All six jars were stirred on the gang stirrer for 10 seconds at 15 RPM and let set for 2 minutes.

3.1.2 Results and Discussion

The data in Table 3 were gathered from the chlorine and hydrogen peroxide jar test during the preliminary experiments.

Table 3. Hydrogen Peroxide and Prefilter Chlorine Jar Test: 31 October 2008

	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
Type	Flume	Flume	Flume + 3ppm H2O2	Flume + 3ppm H2O2	Top of Filter	Top of Filter
pH (pH)	6.60	6.60	6.60	6.60	6.82	6.82
Mn Diss (mg/L)	0.01	0.01	0.09	0.08	0.03	0.03
Mn Total (mg/L)	0.08	0.09	0.10	0.09	0.04	0.04
Fe Diss (mg/L)	0.00	0.00	0.01	0.02	0.00	0.00
Fe Total (mg/L)	0.55	0.50	0.48	0.46	0.11	0.16
TOC (mg/L)	2.45	2.60	2.58	2.41	2.82	2.21
Initial Cl2 (mg/L)	0.00	0.00	0.00	0.00	0.38	0.40
Final Cl2 (mg/L)	0.97	1.02	2.02*	1.05	0.96	0.94

The Imhoff cone was not used for settling water in any other test. Settling will occur in jar tests or in Pittsburgh Water and Sewer Authority Drinking Water Plant's settling ponds. Note that total iron in jars between 1 and 4 is much higher than jars 5 and 6. Further tests suggested that the water settled in an Imhoff cone for 24 hours is not the same as the water coming out of the secondary sedimentation basins. A following set of jar tests were conducted to analyze the flume water that was settled in Imhoff cones and compared it to water that was taken from the top of the filter. The Imhoff Cone jar test procedure results and conclusions are found in Appendix A.

The initial chlorine in jar 5 and 6 registered approximately 0.4 mg/L, this is the prefilter chlorine designed to remove manganese from the drinking water. Above in the discussion about the pH dependence of hydrogen peroxide oxidizing manganese, it was mentioned that at a lower pH values the following reaction will actually reverse.

$$Mn^{2+}_{(aq)} + H_2O_2 \rightarrow MnO_{2(s)} + 2\ H^+$$

All of the jar pH values measured on average 6.71 which were too low to oxidize manganese effectively. Note the difference between jars 3 and 4 dissolved and total manganese and jars 1 and 2 dissolved and total manganese. It shows that the majority of the manganese began as solid manganese, manganese dioxide (MnO_2) and the hydrogen peroxide at low pH actually reduced the manganese to Mn^{2+}. Manganese ion, Mn^{2+}, is the reduced species of manganese and cannot be removed by filtration.

An unforeseen phenomenon occurred during this set of jar tests. A reaction between hydrogen peroxide and the free chlorine took place. In jars 1-4, 10 mL of the working chlorine solution was required to create a 1 mg/L concentration in the 1 Liter jar. For jars 5 and 6, which already had prefilter chlorine in them, only about 5 mL of the working chlorine solution was required to create a 1 mg/L concentration in the 1 Liter jar. In the jars with the 3 mg/L of hydrogen peroxide almost 40 mL of working solution needed to be added. The following reaction explains the phenomenon:

$$OCl^- + H_2O_2 \rightarrow H_2O + O_2 + Cl^-$$

Hydrogen peroxide and free chlorine are both strong oxidants. Table 1 in section 2.5 lists hydrogen peroxide as a stronger oxidant than chlorine. In the above reaction, the free chlorine is being oxidized to a chloride ion and the hydrogen peroxide is being reduced to water and oxygen.

Note that there was a 3:1 ratio of hydrogen peroxide to chlorine, meaning that in jars 3 and 4 there were 3 mg/L of hydrogen peroxide to 1 mg/L of chlorine added. Also note that there was a 1:1 molar ratio of free chlorine to peroxide needed in the above chemical equation. A chlorine reading was taken after every 2-5 mL of working solution added. The results resembled a pH titration curve with buffer. The more chlorine that was added resulted in no additional chlorine being measured with the meter. When approximately 40 mL of working solution were added, then the chlorine reading increased very quickly. Note that 40 mL of working chlorine solution was 4 times the amount of chlorine required by calculation.

The chlorine - hydrogen peroxide reaction will create a large logistic problem for plant operation. Disinfection occurs soon after filtration. In PWSA's drinking water plant there is an 8 hour time before the post filtered water flows out of the clear well. The clear well is where the chlorine for disinfection is added. Since the hydrogen peroxide oxidizes the free chlorine and the chemical reaction yields chloride ion, useless in disinfection, it is not feasible to use hydrogen peroxide so close to chlorine disinfection in the treatment process.

The half life of hydrogen peroxide ranges from 8 hours to 20 days depending on the microbiological activity and metal contamination of the water [FMC Corporation, 2008]. So even if the hydrogen peroxide is added at the head of the treatment works, PWSA's detention time of 3 days is not long enough for the hydrogen peroxide to dissipate and allow the chlorine to disinfect uninhibited.

3.2 HYDROGEN PEROXIDE AT VARYING PH LEVELS

The following jar tests were completed to examine the effects of hydrogen peroxide and the plant levels of potassium permanganate at elevated pH levels. Sources suggest that an elevated pH enhances oxidation of iron and manganese by hydrogen peroxide [U.S. Peroxide, 2005]. It was hypothesized that the increase in the pH will also help oxidize iron and manganese. The mechanism may or may not be due to the potassium permanganate oxidizing more efficiently in alkaline conditions. This experiment tested these hypotheses. The following is the procedure.

3.2.1 Materials and Methods for First Test with a pH Range of 6.8 to 7.6

This test was completed twice to validate results.

1. The prefilter chlorine was off for 3 days
2. 6 Liters of water were taken from the top of the filter on the day of the testing. The filter has been recently backwashed and does NOT contain prefilter chlorine in it.
3. There were 6 -1 Liter beakers filled to be put on the gang stirrer. A description of the six beakers follows:

Table 4. Hydrogen Peroxide Jar Test Setup 1

	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
Actual pH	6.80	6.80	7.20	7.20	7.60	7.60
Hydrogen Peroxide	No	Yes	No	Yes	No	Yes

4. 1 Molar NaOH was used to increase the pH to the desired level.
5. The first step was to dilute 3% store bought hydrogen peroxide to 3mg/L hydrogen peroxide by taking a 10% dilution of H_2O_2 in a separate container (i.e. 10 mL of 3% peroxide into 100 mL solution) and then pipette 1 mL of this working solution into a 1 L jar test to achieve 3 mg/L of 100% H_2O_2.
6. Next, the mixer on all six beakers at 15 RPM for 10 minutes and then add 3 mg/L of hydrogen peroxide to beakers 3 and 4. The 15 RPM mixing replicated the gentle mixing in the flocculation basin.
7. Finally, the 6 beakers had no mixing for 50 minutes for quiescent settling.
8. A sample each beaker of was run on the Atomic Absorption Spectrophotometer (AA) for iron and manganese.
    a. The testing tube for the AA was pre-rinsed in Milli-Q® ultrapure water. The next step was to submerge each tube in one to one nitric acid and then Milli-Q® ultrapure water was used to rinse off the acid. The tubes were handled with plastic forceps so no additional metal contamination took place.
    b. 100 mL of Milli-Q® ultrapure water was put through the 0.45 micrometer filter to ensure there is no residue on the filter before the run.
    c. The dissolved and total levels for Iron and Manganese were recorded.
9. The set up of the 0.45 micrometer filter that was used for the AA sampling was used to simulate filtration for the jar test. The filtered sample was collected in a sanitary flask. This water was used in the following steps of the procedure.
10. Before the test was run, pH and temperature tests were run and recorded.

11. After the experiment, samples for the dissolved and total manganese concentration were collected.
12. Samples for the dissolved and total iron concentration were collected.
13. Samples for total organic carbon were collected.
14. Samples for the UV 254 Absorbance test were collected.

At a later date, the test was repeated and more parameters were monitored. However the second time the test was run, the dose of hydrogen peroxide was doubled to 6 mg/L. The second series of bench-scale tests used a hydrogen peroxide meter to measure the dose and residual of hydrogen peroxide.

3.2.2 Materials and Methods for Second Test with a pH Range of 8.0 to 8.8

This method was completed twice to validate results.

1. The prefilter chlorine will be off for 4 days.
2. 6 Liters of water were taken from the top of the filter on the day of the testing. The filter has been recently backwashed and does NOT contain prefilter chlorine in it.
3. There were 6 -1 Liter beakers filled to be put on the gang stirrer. A description of the six beakers is as follows:

Table 5. Hydrogen Peroxide Jar Test Setup 2

	Jar 1	**Jar 2**	**Jar 3**	**Jar 4**	**Jar 5**	**Jar 6**
Actual pH	8.00	8.00	8.40	8.40	8.80	8.80
Hydrogen Peroxide	No	Yes	No	Yes	No	Yes

4. 1 Molar NaOH was used to increase the pH to the desired level.
5. The first step was to dilute 3% store bought hydrogen peroxide to 3mg/L hydrogen peroxide by taking a 10% dilution of H_2O_2 in a separate container (i.e. 10 mL of 3% peroxide into 100 mL solution) and then pipette 1 mL of this working solution into a 1 L jar test to achieve 3 mg/L of 100% H_2O_2.
6. Next, the mixer on all six beakers at 15 RPM for 10 minutes and then add 3 mg/L of hydrogen peroxide to beakers 3 and 4. The 15 RPM mixing replicated the gentle mixing in the flocculation basin.
7. Finally, the 6 beakers had no mixing for 50 minutes for quiescent settling.
8. A sample each beaker of was run on the Atomic Absorption Spectrophotometer (AA) for iron and manganese.
    a. The testing tube for the AA was pre-rinsed in Milli-Q® ultrapure water. The next step was to submerge each tube in one to one nitric acid and then Milli-Q® ultrapure water was used to rinse off the acid. The tubes were handled with plastic forceps so no additional metal contamination took place.
    b. 100 mL of Milli-Q® ultrapure water was put through the 0.45 micrometer filter to ensure there is no residue on the filter before the run.
    c. The dissolved and total levels for Iron and Manganese were recorded.
9. The set up of the 0.45 micrometer filter that was used for the AA sampling was used to simulate filtration for the jar test. The filtered sample was collected in a sanitary flask. This water was used in the following steps of the procedure.
10. Before the test was run, pH and temperature tests were run and recorded.

11. After the experiment, samples for the dissolved and total manganese concentration were collected.
12. Samples for the dissolved and total iron concentration were collected.
13. Samples for total organic carbon were collected.
14. Samples for the UV 254 Absorbance test were collected.

At a later date, the test was repeated and more parameters were monitored. However the second time the test was run, the dose of hydrogen peroxide was doubled to 6 mg/L. The second series of bench-scale tests used a hydrogen peroxide meter to measure the dose and residual of hydrogen peroxide.

3.2.3 Results and Discussion

The final concentration of manganese both dissolved and total is plotted in Figure 12 against pH level and oxidant added. As a general trend, as the pH is increased, the amount of total and dissolved manganese decreases. Hydrogen peroxide was dosed at 3.0 mg/L for the first jar test and 6.0 mg/L for the second jar test. There was no significant increase of manganese removal or oxidation. The complete data set for the hydrogen peroxide bench-scale experiment at varying pH is found in Appendix B.

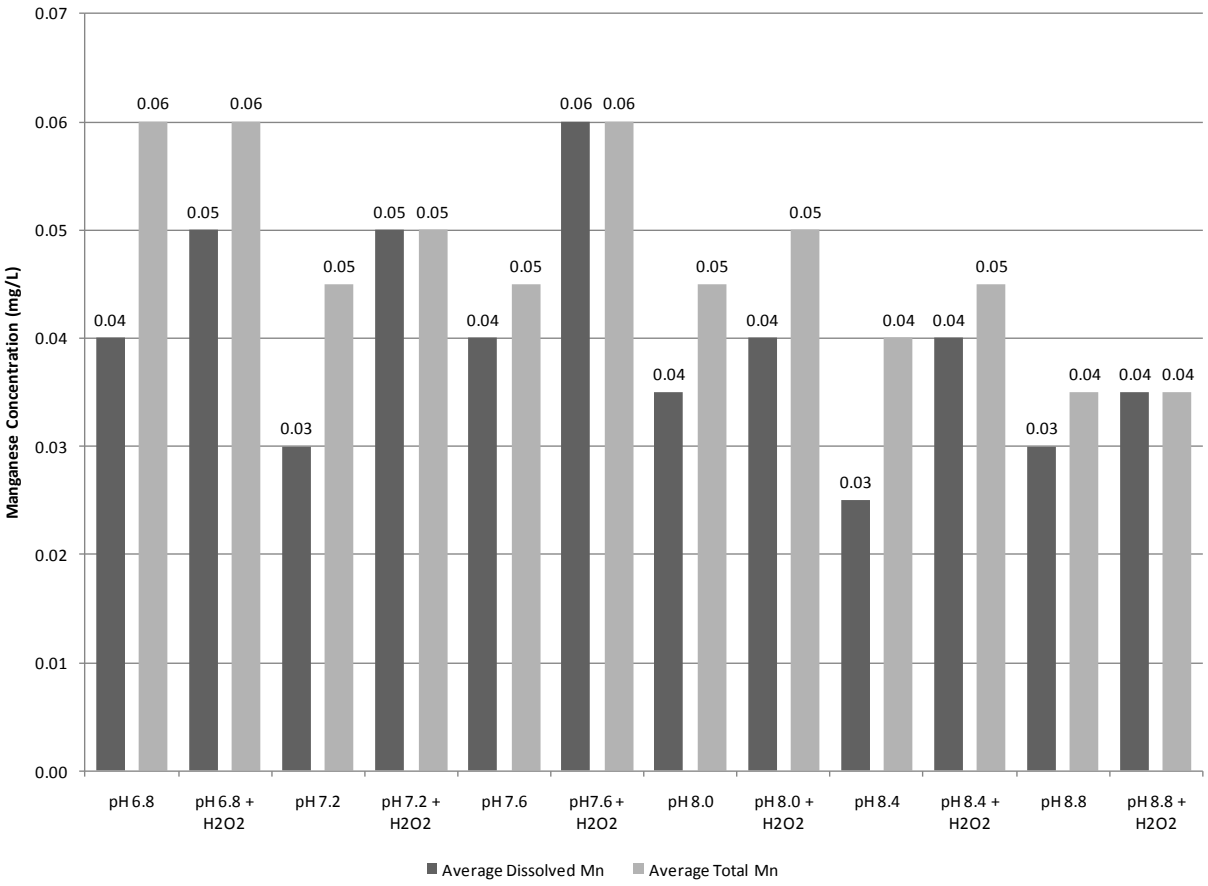

Figure 12. Hydrogen Peroxide and Manganese Concentration at Elevated pH Levels Bench-Scale Study

Table 6 and 7 are summaries of the results from the hydrogen peroxide jar test ranging from the plant pH of 6.8 to 7.6. The majority of manganese present was dissolved and could not be removed in filtration. Hydrogen Peroxide at these pH levels did not prove to be an adequate oxidizing agent for manganese. Iron however was oxidized when hydrogen peroxide was present.

Table 6. Hydrogen Peroxide Jar Test at Varying pH: 12 January 2009

Configuration		Jar 1 pH 6.8	Jar 2 pH 6.8 + H2O2	Jar 3 pH 7.2	Jar 4 pH 7.2 + H2O2	Jar 5 pH 7.6	Jar 6 pH 7.6 + H2O2
Actual pH	**(pH)**	6.85	6.80	7.21	7.17	7.60	7.60
Temp	**(°C)**	6.6	7.1	7.7	8.7	9.0	10.2
Mn Diss	**(mg/L)**	0.04	0.06	0.04	0.05	0.05	0.06
Mn Total	**(mg/L)**	0.06	0.06	0.05	0.05	0.06	0.06
Fe Diss	**(mg/L)**	0.00	0.02	0.02	0.02	0.04	0.00
Fe Total	**(mg/L)**	0.29	0.32	0.21	0.22	0.30	0.29
TOC	**(mg/L)**	1.85	2.60	19.70	6.08	2.44	2.32
UV 254	**(abs.)**	0.018	0.020	0.018	0.012	0.011	0.008

In the second jar test shown in Table 7, the hydrogen peroxide was measured before and after the test. On average only 0.3 mg/L of hydrogen peroxide was consumed in the oxidation process. The 0.3 mg/L is only 5% of the total 6.0 mg/L dosage. It can therefore be concluded that 6.0 mg/L of hydrogen peroxide is an adequate if not excessive dose for oxidation.

Table 7. Hydrogen Peroxide Test at Varying pH: 2 March 2009

Configuration		Jar 1 pH 6.8	Jar 2 pH 6.8 + H2O2	Jar 3 pH 7.2	Jar 4 pH 7.2 + H2O2	Jar 5 pH 7.6	Jar 6 pH7.6 + H2O2
Actual pH	**(pH)**	6.81	6.89	7.15	7.21	7.61	7.60
Temp	**(°C)**	8.6	7.9	8.0	8.2	8.5	9.1
Raw TOC	**(mg/L**	1.25	1.25	1.24	1.20	1.25	1.26
Raw UV 254	**(abs.)**	0.18	0.21	0.17	0.19	0.18	0.18
Raw Turbidity	**(NTU)**	0.58	0.50	0.57	0.52	0.54	0.53
Mn Diss	**(mg/L)**	0.04	0.04	0.02	0.05	0.03	0.06
Mn Total	**(mg/L)**	0.06	0.06	0.04	0.05	0.03	0.06
Fe Diss	**(mg/L)**	0.04	0.00	0.00	0.03	0.00	0.00
Fe Total	**(mg/L)**	0.13	0.19	0.15	0.15	0.10	0.19
Final Turbidity	**(NTU)**	0.25	0.24	0.12	0.11	0.11	0.09
Final H2O2	**(mg/L)**	0.0	6.0	0.0	5.5	0.0	5.5
Final pH	**(pH)**	7.12	6.98	7.11	7.20	7.21	7.41
Final TOC	**(mg/L)**	2.05	1.44	1.49	1.52	1.50	1.53
Final UV 254	**(abs.)**	0.016	0.017	0.013	0.018	0.015	0.018

Results of the hydrogen peroxide jar test at elevated pH results are summarized for both tests in Tables 8 and 9. The test was taken to unpractical pH levels only to have results at a full pH range. Tables 8 and 9 show a decrease in total manganese as pH increases, but what is interesting is that the reduced manganese percentage increases when hydrogen peroxide is present. Once again it is concluded that hydrogen peroxide is not a recommended oxidant for manganese.

Table 8. Hydrogen Peroxide Test at Varying pH: 13 January 2009

Configuration		Jar 1 pH 8.0	Jar 2 pH 8.0 + H2O2	Jar 3 pH 8.4	Jar 4 pH 8.4 + H2O2	Jar 5 pH 8.8	Jar 6 pH 8.8 + H2O2
Actual pH	**(pH)**	7.98	8.02	8.41	8.40	8.86	8.90
Temp	**(°C)**	5.0	8.1	8.9	9.5	10.2	11.0
Mn Diss	**(mg/L)**	0.03	0.03	0.01	0.03	0.03	0.03
Mn Total	**(mg/L)**	0.04	0.04	0.03	0.03	0.03	0.03
Fe Diss	**(mg/L)**	0.00	0.00	0.02	0.01	0.00	0.00
Fe Total	**(mg/L)**	0.12	0.12	0.13	0.20	0.14	0.16
TOC	**(mg/L)**	1.50	1.48	1.47	1.51	1.48	1.49
UV 254	**(abs.)**	0.002	0.002	0.003	0.006	0.004	0.011

Table 9 shows the average use of hydrogen peroxide is 0.83 mg/L which is 14% of the total 6 mg/L dose. At higher pH levels, more hydrogen peroxide is used and more manganese is removed, but still pH levels of 8.4 and 8.8 are impractically high for municipal drinking water production.

Table 9. Hydrogen Peroxide Test at Varying pH: 3 March 2009

Configuration		Jar 1 pH 8.0	Jar 2 pH 8.0 + H2O2	Jar 3 pH 8.4	Jar 4 pH 8.4 + H2O2	Jar 5 pH 8.8	Jar 6 pH 8.8 + H2O2
Actual pH	**(pH)**	7.95	8.03	8.37	8.44	8.83	8.79
Temp	**(°C)**	4.2	4.8	6.1	6.4	6.4	5.9
Raw TOC	**(mg/L**	1.17	1.20	1.25	1.21	1.24	1.20
Raw UV 254	**(abs.)**	0.31	0.32	0.32	0.31	0.33	0.34
Raw Turbidity	**(NTU)**	0.54	0.54	0.52	0.42	0.48	0.51
Mn Diss	**(mg/L)**	0.04	0.05	0.04	0.05	0.03	0.04
Mn Total	**(mg/L)**	0.05	0.06	0.05	0.06	0.04	0.04
Fe Diss	**(mg/L)**	0.00	0.00	0.00	0.00	0.03	0.02
Fe Total	**(mg/L)**	0.14	0.16	0.17	0.14	0.20	0.19
Final Turbidity	**(NTU)**	0.45	0.51	0.33	0.28	0.29	0.41
Final H2O2	**(mg/L)**	0.0	5.0	0.0	6.0	0.0	4.5
Final pH	**(pH)**	7.43	7.63	7.74	7.53	8.16	8.04
Final TOC	**(mg/L)**	1.60	1.59	1.51	1.55	1.73	1.58
Final UV 254	**(abs.)**	0.017	0.023	0.018	0.020	0.018	0.020

The manganese measurement for the Atomic Adsorption Spectrophotometer has an uncertainty range of plus or minus 0.01 mg/L. The minimum detectable concentration of manganese by the AA is 0.01 mg/L. Since the limits detected by the AA are so close to the detection limit, conclusions can be difficult. Even with the level of uncertainty approaching the detection limit, one fact held true. Hydrogen peroxide did not oxidize manganese to manganese dioxide. It actually reduced most of the manganese to Mn^{2+}. Manganese ion can be shown by dissolved manganese reading on the AA.

There does not appear to be a distinct correlation between the addition of hydrogen peroxide and the increase or decrease of TOC. The variance in TOC from jar to jar falls within the normal limits of TOC variance. The pH adjustment did not affect the TOC levels. The UV 254 Absorbance in the raw water was greater or equal to the finished water, however the TOC levels in the raw and finished water do not follow this pattern. In the third test on March 2,

2009, the raw TOC was 1.25 mg/L which is 21% lower than the average of the finished water TOC.

In all tests the raw water turbidity dropped. The lower turbidity shows that the elevated pH and additional time to settle helped to oxidize and settle the metals and other turbid materials. The addition of hydrogen peroxide helped oxidize any ferrous iron left in solution. The hydrogen peroxide did not oxidize the manganese, actually in most cases it actually reduced the manganese and created more Mn^{2+} which is not filterable.

The second time the hydrogen peroxide jar test at varying pH levels were ran, the lab had access to a hydrogen peroxide meter. It is important to note usage of hydrogen peroxide shown. The usage is demonstrated by the difference in hydrogen peroxide in the raw and finished water.

There was more manganese removal at higher pH values. The reasons for more removal is due to most metals oxidize under alkaline conditions. In conclusion there was no benefit to using hydrogen peroxide, it did not oxidize the manganese and it created massive complications width chlorine used for disinfection.

3.3 FERRIC CHLORIDE AND FERRIC SULFATE JAR TEST

Any step used to reduce the amount of manganese being added to the treatment plant after the raw water is introduced is a step worth taking. Ferric chloride from many manufacturers is known to be heavily contaminated with manganese. Up to 5 mg/L of manganese contamination can be present in some brands of ferric chloride, this is ten times the legal amount set forth by the EPA. Ferric sulfate is a coagulant that can be used in enhanced coagulation and contains very low amounts of manganese contamination.

Ferric sulfate was proven by multiple manufacturers to contain less manganese contamination than ferric chloride [States, 2009]. The following experiment looks into the effects of using ferric sulfate as a coagulant and ferric chloride as a coagulant. In jars 3 and 6, there was no potassium permanganate added in order to get an accurate portrayal of how much manganese contamination there is in both coagulants.

3.3.1 Materials and Methods

The following method was completed twice for the sake of duplicity of results.

1. Prefilter chlorination was turned off for 3 days prior to testing.
2. 6 Liters are taken from the raw water inlet.
3. There will be 6 -1 Liter beakers filled to be put on the gang stirrer. The set up looks like this:

Table 10. Ferric Chloride and Ferric Sulfate Setup

	Jar 1	**Jar 2**	**Jar 3**	**Jar 4**	**Jar 5**	**Jar 6**
Coagulant	Ferric Chloride	Ferric Chloride	Ferric Chloride	Ferric Sulfate	Ferric Sulfate	Ferric Sulfate
Potassium Permanganate	Yes	Yes	No	Yes	Yes	No

Jars 1, 2, and 3 contained ferric chloride as a coagulant. Jars 1 and 2 were dosed with permanganate. Jars 4, 5, and 3 contained ferric chloride as a coagulant. Jars 4 and 5 were dosed with permanganate.

4. Take samples of beakers 1-6 and run Fe, Mn, TOC, UV 254 Absorbance, and pH.

5. 0.7 mg/L of potassium permanganate is added to jars 1, 2, 4, and 5. The 0.7 mg/L dose of permanganate was the current recommended dose for PWSA water treatment.
6. 25 mg/L of Ferric Chloride is added to jars 1 – 3.
7. 25 mg/L of Ferric Sulfate is added to jars 4 – 6.
8. The adding of coagulant lowers the pH, so it is necessary to add lime to increase the pH to plant pH of 6.8.
9. A specified amount of calcium carbonate (lime) is added to jars 1-6 to increase the pH to 6.8.
10. Rapid mix for 10 minutes at 100 RPM on the gang stirrer.
11. Coagulate with a medium mix for 10 minutes at 40 RPM on the gang stirrer.
12. Flocculate with a slow mix for 10 minutes at 10 RPM on the gang stirrer.
13. Settle for 30 minutes.
14. Collect samples for Mn dissolved and total.
15. Collect samples for Fe dissolved and total.
16. Take final pH.
17. Collect samples for TOC.
18. Collect samples for UV 254 Absorbance.

3.3.2 Results and Discussion

The following are the data that was obtained over two sets of jar tests testing the effectiveness of ferric sulfate as a coagulant. The results are compared to the more widely used ferric chloride. These jar test results show that there is less manganese contamination in ferric sulfate than ferric chloride. Figure 13 shows both the average raw and average final manganese concentrations. It

should be noted that both jars 3 and 6 contained no potassium permanganate, this was to introduce another control in the experiment. The jars with potassium permanganate contained less final reduced manganese. Ferric sulfate proves to be a cleaner coagulant with less manganese contamination both with and without potassium permanganate oxidation.

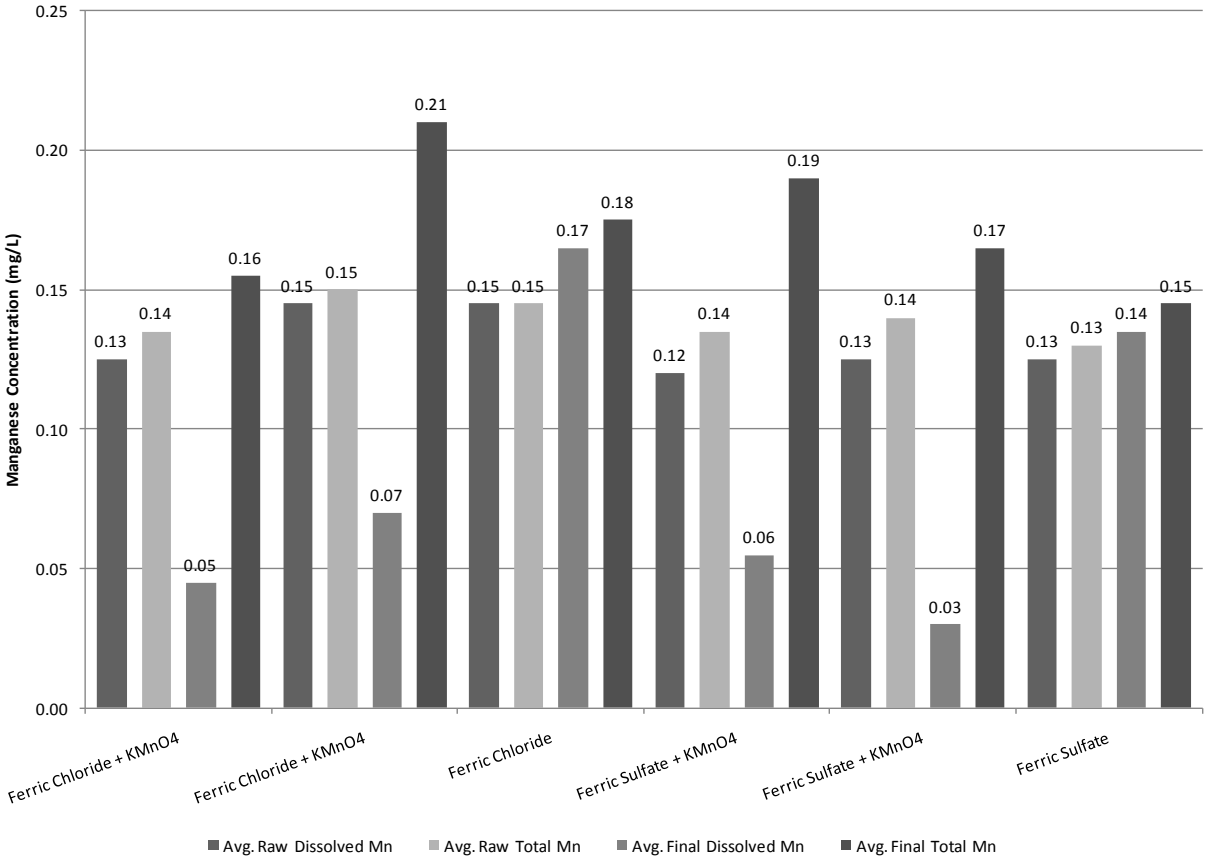

Figure 13. Raw and Final Manganese Concentration Using Ferric Chloride and Ferric Sulfate as Coagulants Bench-Scale Study

Figure 14 is a graph that shows both the average raw and average final iron concentrations. It should be noted that both jars 3 and 6 contained no potassium permanganate, this was to introduce another control in the experiment. Both coagulants, ferric chloride and ferric sulfate use the same mechanism for coagulation, trivalent iron. The atomic weight of iron is 55.845 g/mol. The chemical formula for ferric chloride is $FeCl_3$ and the chemical formula for ferric sulfate is $Fe_2(SO_4)_3$. Gram for gram, ferric chloride is 34% iron and ferric sulfate is 30% iron. Both ferric chloride and ferric sulfate used the same dosage of 25 mg/L. Ferric sulfate is a more expensive coagulant than ferric chloride [States, 2009] and requires a larger dosage due to its molar weight and percentage of trivalent iron. Figure 14 shows the final total iron concentration in ferric sulfate is lower than ferric chloride.

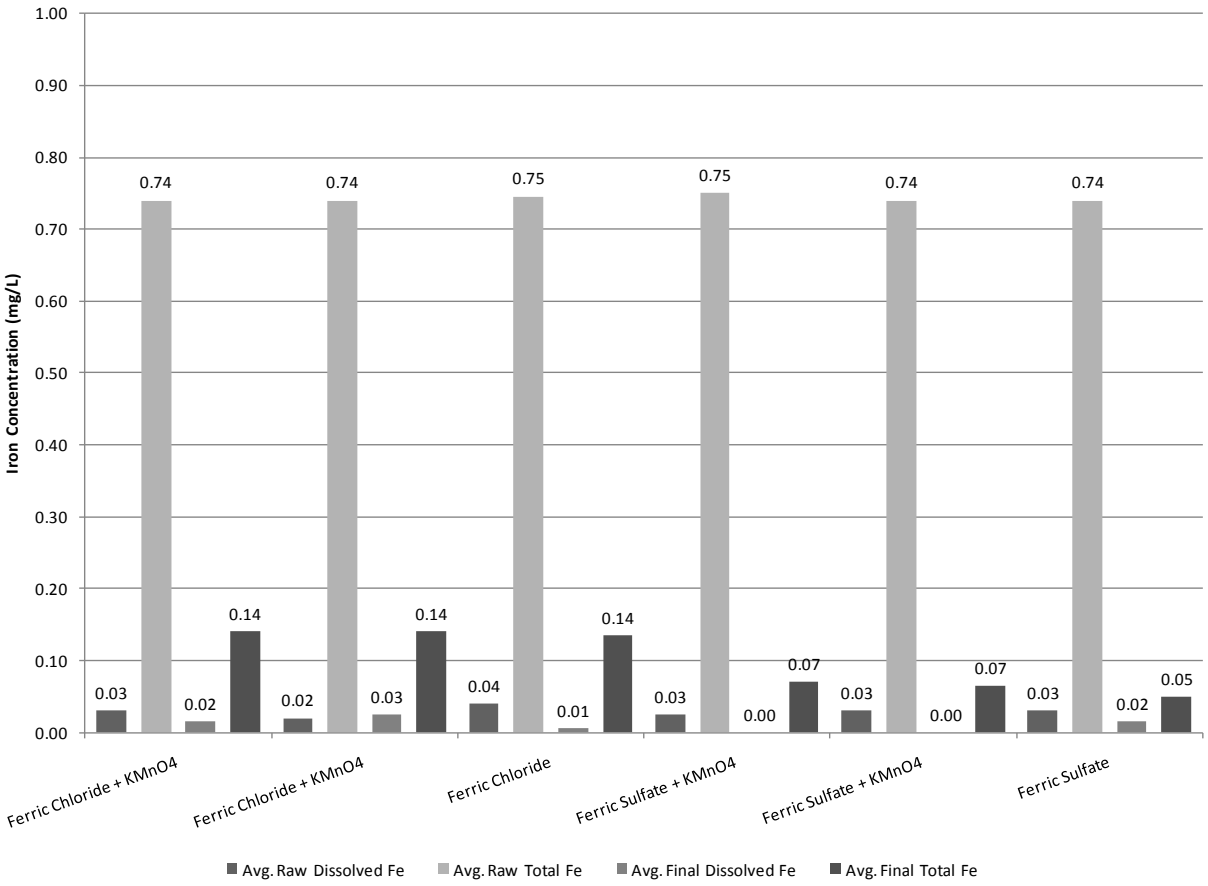

Figure 14. Raw and Final Iron Concentration Using Ferric Chloride and Ferric Sulfate as Coagulants Bench-Scale Study

Additional results and data for the ferric chloride ferric sulfate jar tests can be found in the Appendix.

The raw water in both tests was sufficiently poor. The total iron concentration was on average 0.74 mg/L and the manganese was 0.14 mg/L. Most of the manganese was in its reduced state and dissolved. Since these jar tests represent the treatment process from raw water intake to coagulation, flocculation and to sedimentation; the key is to reduce the amount of total iron and manganese and any that is remaining oxidize it so it is not dissolved. Iron and manganese that is not dissolved will be filtered out in the multi-media filter.

In the first test conducted on February 12, 2009, jars 1, 2, 4, and 5 all showed elevated levels of total manganese. The elevated manganese concentration is probably due to the potassium permanganate added. Jars 3 and 6 did not have the elevated amount of manganese however in jars 3 and 6, 100% of the manganese was dissolved. Potassium permanganate is a strong oxidant and oxidize any manganese from the ionic/dissolved form of Mn^{2+} to the solid oxidized form of MnO_2.

The potassium permanganate successfully oxidized the manganese present in both ferric chloride and ferric sulfate environments. Since permanganate can add manganese to the water, jars 3 and 6 will be analyzed to decide how much excess manganese there is in each type of coagulant. In the raw water there is 0.16 mg/L total manganese. In jar 3 that contains the ferric chloride without potassium permanganate added, there was 0.21 mg/L of total manganese. In jar 6 which contained the ferric sulfate coagulant without potassium permanganate there was 0.18 mg/L of total manganese. In jar 3 with ferric chloride, there was a 0.05 mg/L of total manganese increase. One should note that 0.05 mg/L of manganese is the EPA secondary limit for drinking water. Ferric chloride added enough manganese to exceed the limit on its own. In jar 6 with ferric sulfate, there was a 0.02 mg/L of total manganese increase.

In the second test conducted on 2/16/2009, the oxidation of manganese by permanganate did not occur as hypothesized. Both tests used the same dosage of potassium permanganate and the respective coagulant. Both tests were adjusted to the same pH value. However, there was less total manganese in the raw water and perhaps the permanganate dose was too high and thus creating excess manganese ion. If the dose of potassium permanganate is too high, the permanganate breaks down to Mn^{2+}.

The balance of controlling the potassium permanganate dosage is a complex one that requires constant monitoring and adjustment. The real question that this jar test set out to answer is whether there is more manganese contamination in ferric chloride or ferric sulfate.

In the second week of jar tests that took place on February 16, 2009 there was 0.11 mg/L of total manganese in the raw water. In Jar 6 that contained ferric sulfate as a coagulant there was 0.11 mg/L of total manganese which is a 0% increase in manganese. In jar 3 which used ferric chloride as a coagulant, the total manganese was 0.14 mg/L of total manganese which is 0.3 mg/L increase in manganese. The 0.3 mg/L increase is 60% of the EPA limit for manganese contamination.

Despite the potassium permanganate failing to oxidize the manganese in the second jar test, it is proven that ferric sulfate contains less manganese contamination. Therefore if a utility were to use ferric sulfate as a coagulant, there would be less manganese to remove and one could decrease the dose of prefilter chlorine or even not use it all together.

3.4 LIQUID PERMANGANATE JAR TEST WITH VARYING DOSAGE

Sodium permanganate is a strong oxidant in liquid form and can be dosed at the top of the filter to aid in manganese oxidation and removal through filtration. Sodium permanganate works the same way that potassium permanganate works except that sodium permanganate is always dissolved in water and does not come in crystalline form. In this set of jar tests, the dosage of permanganate was systematically increased and honed in on the optimal dose. The optimal dose was achieved by a series of three jar tests, each one getting more precise and closer to the optimal dosage.

3.4.1 Materials and Methods

The following method was completed three times in lessening variance to accurately approach the correct sodium permanganate dosage.

1. The prefilter chlorine was off for 3 days.
2. 6 Liters of water were taken from the top of the filter on the day of the testing. The filter has been recently backwashed and does NOT contain prefilter chlorine in it.
3. In the first experiment there were 6 - 1 Liter beakers filled to be put on the gang stirrer. A description of the six beakers is as follows:

Table 11. Sodium Permanganate Jar Test 1 Setup

Condition	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
NaMnO4 (mg/L)	0.00	0.20	0.40	0.60	0.80	1.00
Condition	Plant pH	Plant pH	Plant pH	Plant pH	Plant pH	Plant pH

All 6 jars used the same plant pH and were not adjusted with acid or caustic. The range of sodium permanganate concentrations ranged from 0.00 mg/L to 1.00 mg/L. Each jar was stepped by a 0.20 mg/L increment. All other aspects of the procedure are identical.

4. In the second experiment there were 6 - 1 Liter beakers filled to be put on the gang stirrer. A description of the six beakers is as follows:

Table 12. Sodium Permanganate Jar Test Setup 2

Condition	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
NaMnO4 (mg/L)	0.00	0.10	0.20	0.30	0.40	0.50
Condition	Plant pH	Plant pH	Plant pH	Plant pH	Plant pH	Plant pH

All 6 jars used the same plant pH and were not adjusted with acid or caustic. The range of sodium permanganate concentrations ranged from 0.00 mg/L to 0.50 mg/L. Each jar was stepped by a 0.10 mg/L increment. All other aspects of the procedure are identical.

5. In the third experiment there were 6 - 1 Liter beakers filled to be put on the gang stirrer. A description of the six beakers is as follows:

Table 13. Sodium Permanganate Jar Test Setup 3

Condition	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
NaMnO4 (mg/L)	0.00	0.05	0.10	0.15	0.20	0.25
Condition	Plant pH	Plant pH	Plant pH	Plant pH	Plant pH	Plant pH

All 6 jars used the same plant pH and were not adjusted with acid or caustic. The range of sodium permanganate concentrations ranged from 0.00 mg/L to 0.25 mg/L. Each jar was stepped by a 0.05 mg/L increment. All other aspects of the procedure are identical.

6. The stock solution of sodium permanganate is a 20% concentration and has a molecular weight of 142 gram/mole. To determine the molarity of the stock solution, the following equation was used.

$$\left(\frac{200{,}000\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 1.40845\ mol/L$$

To achieve a dilute solution of 1000 mg/L, the following equation was used.

$$\left(\frac{1000\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 0.0070422\ mol/L$$

Take 1 mL of stock solution and dilute it to a 1000 mg/L solution using the following equation.

$$M_1V_1 = M_2V_1$$

$$\left(1.40845\,\frac{mol}{L}\right) \times (0.005L) = \left(0.0070422\,\frac{mol}{L}\right) \times (\alpha\ L)$$

$$\alpha = 1\ L$$

Place 5 mL of stock solution into a 1L flask and fill the flask with deionized water. The result is working solution 1 and has a 1000 mg/L concentration.

To achieve a dilute solution of 100 mg/L, the following equation was used.

$$\left(\frac{100\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 7.0422 \times 10^{-4}\ mol/L$$

Take 100 mL of working solution 1 (1000 mg/L) and dilute it to a 100 mg/L solution using the following equation.

$$M_1V_1 = M_2V_1$$

$$\left(0.0070422\,\frac{mol}{L}\right) \times (0.100\ L) = \left(7.0422 \times 10^{-4}\,\frac{mol}{L}\right) \times (\beta\ L)$$

$$\beta = 1\ L$$

Place 100 mL of working solution 1 (1000 mg/L) into a 1 L flask and fill the flask with deionized water. The result is working solution 2 and has a 100 mg/L concentration. The second working solution is the solution that will be dosed into the jar to attain the correct concentration of sodium permanganate.

To attain a 0.1 mg/L concentration in the jar, 1 mL of working solution 2 was added to the jar. This is proved by the following equations.

$$\left(\frac{0.1\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 7.0422 \times 10^{-7}\ mol/L$$

Take 1 mL of working solution 1 (1000 mg/L) and dilute it to a 1 mg/L solution using the following equation.

$$M_1V_1 = M_2V_1$$

$$\left(7.0422 \times 10^{-4}\,\frac{mol}{L}\right) \times (x\ L) = \left(7.0422 \times 10^{-7}\,\frac{mol}{L}\right) \times (1\ L)$$

$$x = 0.001\ L = 1\ mL$$

a. For Jar 1 there is no working solution 1 of sodium permanganate added to achieve a concentration of 0 mg/L sodium permanganate.
b. For Jar 2 there is 2 mL of working solution 1 of sodium permanganate added to achieve a concentration of 0.2 mg/L sodium permanganate.
c. For Jar 3 there is 4 mL of working solution 1 of sodium permanganate added to achieve a concentration of 0.4 mg/L sodium permanganate.
d. For Jar 4 there is 6 mL of working solution 1 of sodium permanganate added to achieve a concentration of 0.6 mg/L sodium permanganate.
e. For Jar 5 there is 8 mL of working solution 1 of sodium permanganate added to achieve a concentration of 0.8 mg/L sodium permanganate.
f. For Jar 6 there is 10 mL of working solution 1 of sodium permanganate added to achieve a concentration of 1.0 mg/L sodium permanganate.

Note that the same ratios are used for the second and third experiments.

7. Next, the mixers on all six beakers were set to 100 RPM for 5 minutes to rapid mix and then the appropriate amount of sodium permanganate is added.
8. The mixers on all six beakers are reduced to 40 RPM for 5 minutes to flocculate.
9. Finally, the 6 beakers quiescently settled for 40 minutes.
10. A sample each beaker of was run on the Atomic Absorption instrument (AA) for Iron and Manganese.

a. The testing tube for the AA was pre-rinsed in Milli-Q® ultrapure water. The next step was to submerge each tube in one to one nitric acid and then Milli-Q® ultrapure water was used to rinse off the acid. The tubes were handled with plastic forceps so no additional metal contamination took place.
b. 100 mL of Milli-Q® ultrapure water was put through the 0.45 micrometer filter to ensure there is no residue on the filter before the run.
c. The dissolved and total levels for Iron and Manganese were recorded.

11. The set up of the 0.45 micrometer filter that was used for the AA sampling was used to simulate filtration for the jar test. The filtered sample was collected in a sanitary flask. This water was used in the following steps of the procedure.
12. Before the test was run, a series of tests were run on the untreated water. These include:
    a. Actual pH
    b. Raw Turbidity
    c. Raw Dissolved and Total Manganese Concentration
    d. Raw Dissolved and Total Iron Concentration
13. After the experiment, a series of tests were run on the untreated water. These include:
    a. Final pH
    b. Final Turbidity
    c. Dissolved and Total Manganese Concentration
    d. Dissolved and Total Iron Concentration

3.4.2 Results and Discussion

Figure 15 relates the sodium permanganate dose and the resulting concentration of dissolved manganese. The figure below is an example of the manganese break through curve that occurs when permanganate is used to remove manganese from drinking water. When there is too little oxidant dosed, the dissolved manganese concentration is high, when the dose is optimized, there is no dissolved manganese present and when the dose is too high, dissolved manganese passes through in the form of permanganate.

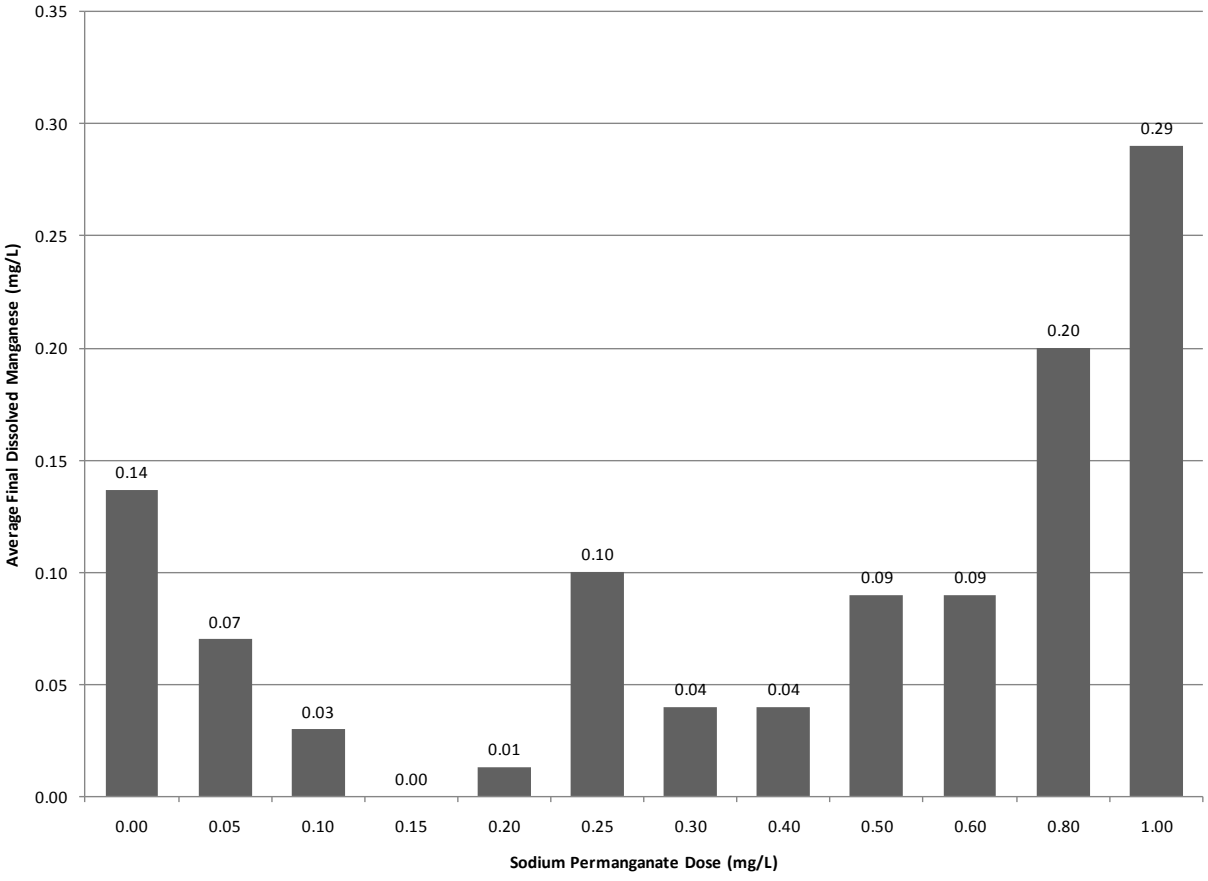

Figure 15. Sodium Permanganate Dose and Concentration of Dissolved Manganese Bench-Scale Study

Table 14 contains the results from the first of the three successive jar tests. The first test had the most variance in dosage from 0.00 mg/L of sodium permanganate to 1.00 mg/L of sodium permanganate. In the subsequent two jar tests, iron concentration was also analyzed. Using this large variation in dosages, the 0.20 and 0.40 mg/L dose prove to be the most optimized. The final total manganese concentration is not as critical as the reduced or dissolved concentration. This is because, only the dissolved manganese will pass through the filter, all of the rest (oxidized) manganese will be removed during filtration. It should be noted that excessive amounts of total manganese will increase the frequency of filter backwashes because of greater filter loading.

Table 14. Sodium Permanganate Jar Test 1: 22 April 2009

		Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
NaMnO4 Dose	**(mg/L)**	**0.0**	**0.2**	**0.4**	**0.6**	**0.8**	**1.0**
Raw pH	**(pH)**	6.79	6.80	6.80	6.91	6.74	6.77
Raw Turbidity	**(NTU)**	0.607	0.591	0.880	0.624	1.13	0.976
Raw Dissolved Mn	**(mg/L)**	0.16	0.15	0.16	0.15	0.15	0.16
Raw Total Mn	**(mg/L)**	0.16	0.16	0.16	0.15	0.16	0.16
Final pH	**(pH)**	7.21	7.09	7.09	7.16	7.06	7.10
Final Turbidity	**(mg/L)**	0.357	0.187	0.463	0.320	0.319	0.624
Final Dissolved Mn	**(mg/L)**	0.16	0.02	0.03	0.09	0.20	0.29
Final Total Mn	**(mg/L)**	0.16	0.26	0.33	0.37	0.50	0.60
Color	**(Color)**	Clear	Yellow	Yellow	Light Pink	Pink	Very Pink

Table 15 was based on the results of Table 14. As discussed above, the ideal dosage for sodium permanganate was between 0.20 and 0.40 mg/L. To attain a more precise optimized permanganate dosage, the second jar test only varied from 0.00 mg/L to 0.50 mg/L. The second jar test still used all 6 jars, so the step between each jar was 0.10 mg/L of dosage. Here, the optimum dose lied between 0.10 mg/L and 0.20 mg/L which could not have been determined in the first jar test.

Table 15. Sodium Permanganate Jar Test 2: 23 April 2009

NaMnO4 Dose	(mg/L)	Jar 1 0.0	Jar 2 0.1	Jar 3 0.2	Jar 4 0.3	Jar 5 0.4	Jar 6 0.5
Raw pH	**(pH)**	7.01	6.96	6.94	6.98	7.00	6.99
Raw Turbidity	**(NTU)**	0.83	0.746	0.901	0.648	0.821	0.964
Raw Dissolved Mn	**(mg/L)**	0.13	0.13	0.12	0.13	0.12	0.13
Raw Total Mn	**(mg/L)**	0.13	0.13	0.12	0.14	0.12	0.13
Raw Dissolved Fe	**(mg/L)**	0.00	0.01	0.00	0.00	0.00	0.00
Raw Total Fe	**(mg/L)**	0.23	0.25	0.21	0.23	0.23	0.24
Final pH	**(pH)**	7.13	7.11	7.20	7.12	7.11	7.06
Final Turbidity	**(mg/L)**	0.141	0.191	0.52	0.245	0.207	0.348
Final Dissolved Mn	**(mg/L)**	0.13	0.03	0.02	0.04	0.05	0.09
Final Total Mn	**(mg/L)**	0.13	0.18	0.23	0.26	0.31	0.34
Final Dissolved Fe	**(mg/L)**	0.01	0.00	0.00	0.00	0.00	0.00
Final Total Fe	**(mg/L)**	0.14	0.14	0.18	0.11	0.16	0.12
Color	**(Color)**	Clear	Clear	Light Yellow	Yellow	Light Brown	Light Pink

Table 16 was based on the results of Table 15. As discussed above, the ideal dosage for sodium permanganate was between 0.10 and 0.20 mg/L. To attain a more precise optimized permanganate dosage, the second jar test was devised and only varied from 0.00 mg/L to 0.25 mg/L. The third jar test still used all 6 jars, so the step between each jar was 0.05 mg/L of dosage. Here, the optimum dose lied between 0.15 mg/L and 0.20 mg/L which could not have been determined in the first or second jar test.

Table 16. Sodium Permanganate Jar Test 3: 23 April 2009

NaMnO4 Dose	(mg/L)	Jar 1 0.00	Jar 2 0.05	Jar 3 0.10	Jar 4 0.15	Jar 5 0.20	Jar 6 0.25
Raw pH	**(pH)**	6.92	6.99	6.94	6.92	6.94	6.94
Raw Turbidity	**(NTU)**	1.14	1.02	1.14	1.02	1.77	0.764
Raw Dissolved Mn	**(mg/L)**	0.13	0.12	0.13	0.13	0.12	0.13
Raw Total Mn	**(mg/L)**	0.13	0.13	0.14	0.13	0.12	0.13
Raw Dissolved Fe	**(mg/L)**	0.00	0.00	0.00	0.00	0.00	0.01
Raw Total Fe	**(mg/L)**	0.16	0.17	0.15	0.16	0.16	0.18
Final pH	**(pH)**	7.10	7.17	7.19	7.14	7.14	7.20
Final Turbidity	**(mg/L)**	0.274	0.217	0.329	0.475	0.22	0.314
Final Dissolved Mn	**(mg/L)**	0.12	0.07	0.03	0.00	0.00	0.01
Final Total Mn	**(mg/L)**	0.14	0.14	0.16	0.18	0.20	0.21
Final Dissolved Fe	**(mg/L)**	0.02	0.02	0.02	0.00	0.00	0.01
Final Total Fe	**(mg/L)**	0.15	0.15	0.12	0.10	0.14	0.15
Color	**(Color)**	Clear	Clear	Light Light Yellow	Light Yellow	Light Yellow	Yellow

The color evaluation shown above in the last row of the jar test data is simple and relatively accurate way of measuring the manganese concentration. As shown above, the spectrum of manganese concentrations ranges from clear, to light yellow, to yellow, to light brown or tea colored, to light pink, and finally to bright pink. Since permanganate treatment does not work if the chemical was under-dosed or overdosed, it was imperative to conduct the jar tests over a range of permanganate concentrations. These ranges got smaller and smaller with each successive test to approximate to the 0.05 mg/L dose required to oxidize all of the manganese and not add additional manganese that would pass through the filter.

The first jar test ranged from 0.00 mg/L to 1.00 mg/L in 0.20 mg/L increments. The correct dosage was found when the least amount of dissolved manganese is detected. From the first jar test, the dosage of 0.20 mg/L and 0.40 mg/L resulted in the least amount of reduced or dissolved manganese.

The second jar test attempted to further isolate the correct dosage. The second jar test ranged from 0.00 mg/L to 0.50 mg/L in 0.10 step increments. Judging from the color alone a clear to yellow color indicates the correct amount of manganese. Results from the Atomic Absorption Spectrophotometer indicate that jars 2, 3, and 4 had the least amount of reduced manganese. Jars 2 through 4 ranged from 0.10 mg/L to 0.30 mg/L. A further more specific test was run to narrow down the correct dosage to nearest 0.05 mg/L.

The third jar test ranged from 0.00 mg/L to 0.25 mg/L with a step increment of 0.05 mg/L. This increment is approaches the dosing limitations of PWSA's equipment. Further jar tests could have been preformed, but any more precise doses would not have been able to be duplicated in the field. The ideal dosage is between 0.15 mg/L and 0.20 mg/L. All three jar tests confirmed the ideal dosage being between 0.15 and 0.20 mg/L.

3.5 ELEVATED PH PREFILTER CHLORINE JAR TEST

Any means taken to reduce the amount of prefilter chlorine required for oxidizing iron and manganese is a step toward optimizing the water treatment plant. The Pourbaix diagram (Figure 4) in section 2.3, shows that manganese is more easily oxidized at higher pH levels. The thought behind this preliminary jar test was to use reduced amount of chlorine to oxidize manganese but do so in an elevated pH atmosphere.

3.5.1 Materials and Methods for First Test with a pH Range of 6.8 to 7.6

1. The treatment plant prefilter chlorine was off for 3 days.

2. 6 Liters of water were taken from the top of the filter on the day of the testing. The filter has been recently backwashed and does NOT contain prefilter chlorine in it.
3. There were 6 -1 Liter beakers filled to be put on the gang stirrer. A description of the six beakers follows:

Table 17. Elevated pH Prefilter Chlorine Setup 1

	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
Actual pH	6.8	6.8	7.2	7.2	7.6	7.6
Total Chlorine Dose (mg/L)	0.2	0.2	0.2	0.2	0.2	0.2

4. 1 Molar NaOH was used to increase the pH to the desired level.
5. Enough dilute plant grade sodium hypochlorite was added to attain a total chlorine concentration of 0.2 mg/L. The dosing and dilution depends on the strength of the stock solution which can vary between 10% and 16%. A series of checks were put into place to test the stock solution and ensure the correct dosage in each 1 L jar. The jar was tested for total chlorine just as the dose was added and after the test was completed to determine a chlorine demand for each jar.
6. Next, the mixer on all six beakers at 15 RPM for 10 minutes The 15 RPM mixing replicated the gentle mixing in the flocculation basin.
7. Finally, the 6 beakers had no mixing for 30 minutes for quiescent settling.
8. A sample each beaker of was run on the Atomic Absorption instrument (AA) for Iron and Manganese.

a. The testing tube for the AA was pre-rinsed in Milli-Q® ultrapure water. The next step was to submerge each tube in one to one nitric acid and then Milli-Q® ultrapure water was used to rinse off the acid. The tubes were handled with plastic forceps so no additional metal contamination took place.
b. 100 mL of Milli-Q® ultrapure water was put through the 0.45 micrometer filter to ensure there is no residue on the filter before the run.
c. The dissolved and total levels for Iron and Manganese were recorded.

9. The set up of the 0.45 micrometer filter that was used for the AA sampling was used to simulate filtration for the jar test. The filtered sample was collected in a sanitary flask. This water was used in the following steps of the procedure.
10. Before the test was run, pH and temperature tests were run and recorded.
11. After the experiment, samples for the dissolved and total manganese concentration were collected.
12. Samples for the dissolved and total iron concentration were collected.
13. Samples for total organic carbon were collected.
14. Samples for the UV 254 Absorbance test were collected.

3.5.2 Materials and Methods for Second Test with a pH Range of 8.0 to 8.8

1. The prefilter chlorine was off for 4 days.
2. 6 Liters of water were taken from the top of the filter on the day of the testing. The filter has been recently backwashed and does NOT contain prefilter chlorine in it.
3. There were 6 -1 Liter beakers filled to be put on the gang stirrer. A description of the six beakers follows:

Table 18. Elevated pH Prefilter Chlorine Setup 2

	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
Actual pH	8.0	8.0	8.4	8.4	8.8	8.8
Total Chlorine Dose (mg/L)	0.2	0.2	0.2	0.2	0.2	0.2

4. 1 Molar NaOH was used to increase the pH to the desired level.
5. Enough dilute plant grade sodium hypochlorite was added to attain a total chlorine concentration of 0.2 mg/L. The dosing and dilution depends on the strength of the stock solution which can vary between 10% and 16%. A series of checks were put into place to test the stock solution and ensure the correct dosage in each 1 L jar. The jar was tested for total chlorine just as the dose was added and after the test was completed to determine a chlorine demand for each jar.
6. Next, the mixer on all six beakers at 15 RPM for 10 minutes The 15 RPM mixing replicated the gentle mixing in the flocculation basin.
7. Finally, the 6 beakers had no mixing for 30 minutes for quiescent settling.
8. A sample each beaker of was run on the Atomic Absorption instrument (AA) for Iron and Manganese.
    a. The testing tube for the AA was pre-rinsed in Milli-Q® ultrapure water. The next step was to submerge each tube in one to one nitric acid and then Milli-Q® ultrapure water was used to rinse off the acid. The tubes were handled with plastic forceps so no additional metal contamination took place.

b. 100 mL of Milli-Q® ultrapure water was put through the 0.45 micrometer filter to ensure there is no residue on the filter before the run.
c. The dissolved and total levels for Iron and Manganese were recorded.

9. The set up of the 0.45 micrometer filter that was used for the AA sampling was used to simulate filtration for the jar test. The filtered sample was collected in a sanitary flask. This water was used in the following steps of the procedure.
10. Before the test was run, pH and temperature tests were run and recorded.
11. After the experiment, samples for the dissolved and total manganese concentration were collected.
12. Samples for the dissolved and total iron concentration were collected.
13. Samples for total organic carbon were collected.
14. Samples for the UV 254 Absorbance test were collected.

3.5.3 Results and Discussion

The figure below shows the results from the elevated pH prefilter chlorine jar test. The average dose for prefilter chlorination falls between 0.30 and 0.50 mg/L of total chlorine required to oxidize manganese for removal on the multimedia filters. The purpose of this experiment was to limit the amount of chlorine necessary to oxidize manganese by increasing the pH level. Metals in solution at higher pH levels are more apt to oxidize than those in acidic conditions. Below in figure 16, the dose of 0.20 mg/L of total chlorine was not sufficient in oxidizing enough manganese. The concentration of manganese in the water is in violation with EPA's secondary drinking water standards of 0.05 mg/L total manganese concentration. The increase in pH, does

not appear to aid in the chlorine oxidation. The entire reduced dose prefilter chlorine bench-scale tests at varying pH data is found in Appendix D.1.

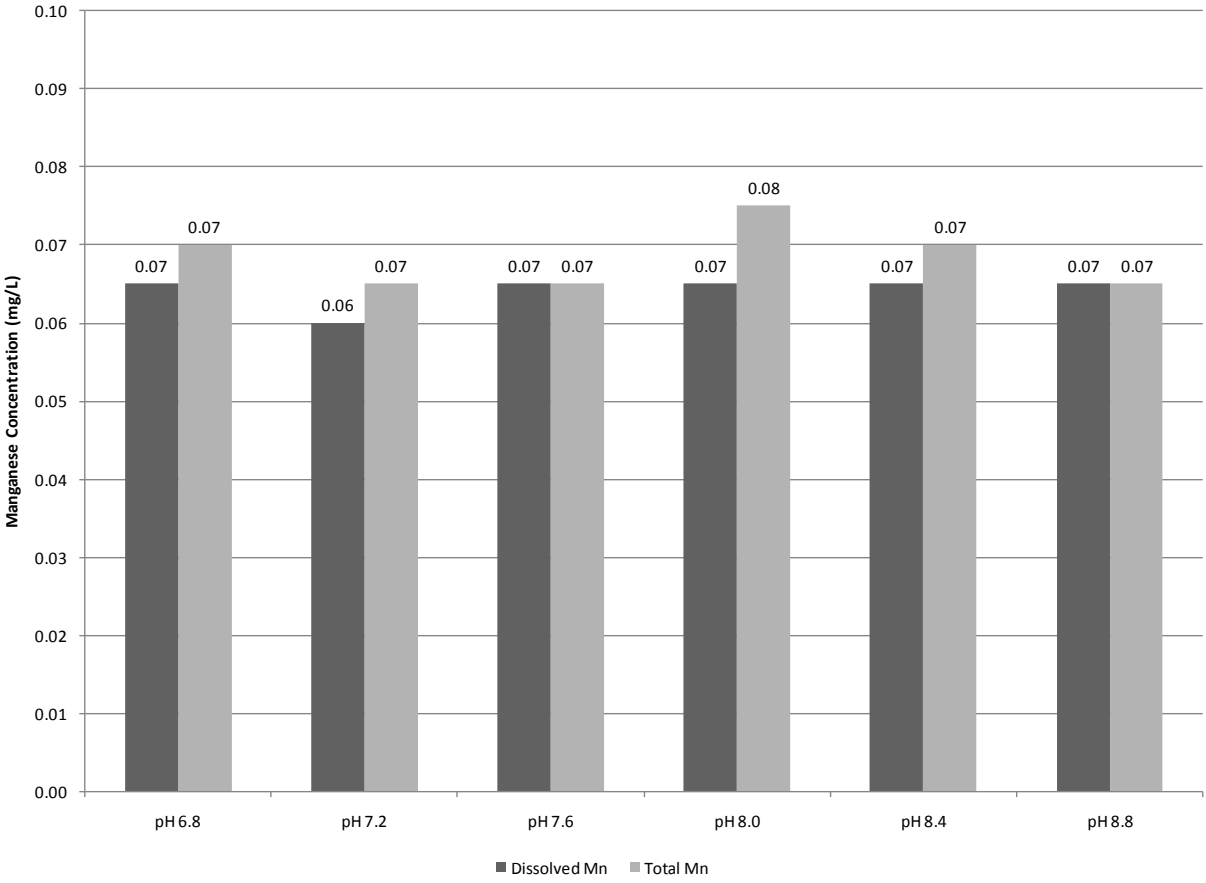

Figure 16. Elevated pH Prefilter Chlorine Dose 0.2 mg/L (Reduced Chlorine Dose) Bench-Scale Study

3.6 ELEVATED PH LIQUID PERMANGANATE JAR TEST

There is an operational risk of overdosing permanganate when adding the chemical before the filters. There is not much room for error, the dose needs to be correct and the dose required can change often depending on raw water quality or changes in treatment. The Pourbaix diagram (Figure 4) in section 2.3, shows that manganese is more easily oxidized at higher pH levels. The

purpose behind this preliminary jar test was to use reduced amount of permanganate needed to oxidize manganese but do so in an elevated pH atmosphere.

3.6.1 Materials and Methods for First Test with a pH Range of 6.8 to 7.6

1. The prefilter chlorine was off for 3 days.
2. 6 Liters of water were taken from the top of the filter on the day of the testing. The filter has been recently backwashed and does NOT contain prefilter chlorine in it.
3. There were 6 -1 Liter beakers filled to be put on the gang stirrer. A description of the six beakers follows:

Table 19. Elevated pH Prefilter Permanganate Dose Setup 1

	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
Actual pH	6.8	6.8	7.2	7.2	7.6	7.6
Sodium Permanganate Dose (mg/L)	0.1	0.1	0.1	0.1	0.1	0.1

4. 1 Molar NaOH was used to increase the pH to the desired level.
5. The stock solution of sodium permanganate is a 20% concentration and has a molecular weight of 142 gram/mole. To determine the molarity of the stock solution, the following equation was used.

$$\left(\frac{200{,}000\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 1.40845\ mol/L$$

To achieve a dilute solution of 1000 mg/L, the following equation was used.

$$\left(\frac{1000\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 0.0070422\ mol/L$$

Take 1 mL of stock solution and dilute it to a 1000 mg/L solution using the following equation.

$$M_1V_1 = M_2V_1$$

$$\left(1.40845\frac{mol}{L}\right) \times (0.005L) = \left(0.0070422\frac{mol}{L}\right) \times (\alpha\ L)$$

$$\alpha = 1\ L$$

Place 5 mL of stock solution into a 1L flask and fill the flask with deionized water. The result is working solution 1 and has a 1000 mg/L concentration.

To achieve a dilute solution of 100 mg/L, the following equation was used.

$$\left(\frac{100\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 7.0422 \times 10^{-4}\ mol/L$$

Take 100 mL of working solution 1 (1000 mg/L) and dilute it to a 100 mg/L solution using the following equation.

$$M_1V_1 = M_2V_1$$

$$\left(0.0070422\frac{mol}{L}\right) \times (0.100\ L) = \left(7.0422 \times 10^{-4}\frac{mol}{L}\right) \times (\beta\ L)$$

$$\beta = 1\ L$$

Place 100 mL of working solution 1 (1000 mg/L) into a 1 L flask and fill the flask with deionized water. The result is working solution 2 and has a 100 mg/L concentration. The second working solution is the solution that will be dosed into the jar to attain the correct concentration of sodium permanganate.

To attain a 0.1 mg/L concentration in the jar, 1 mL of working solution 2 was added to the jar. This is proved by the following equations.

$$\left(\frac{0.1\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 7.0422 \times 10^{-7}\ mol/L$$

Take 1 mL of working solution 1 (1000 mg/L) and dilute it to a 1 mg/L solution using the following equation.

$$M_1V_1 = M_2V_1$$

$$\left(7.0422 \times 10^{-4}\frac{mol}{L}\right) \times (x\ L) = \left(7.0422 \times 10^{-7}\frac{mol}{L}\right) \times (1\ L)$$

$$x = 0.001\ L = 1\ mL$$

For all 6 jars, 1.0 mL of working solution 1 of sodium permanganate added to achieve a concentration of 0.10 mg/L sodium permanganate.

6. Next, the mixer on all six beakers at 15 RPM for 10 minutes The 15 RPM mixing replicated the gentle mixing in the flocculation basin.
7. Finally, the 6 beakers had no mixing for 30 minutes for quiescent settling.
8. A sample each beaker of was run on the Atomic Absorption instrument (AA) for Iron and Manganese.
    a. The testing tube for the AA was pre-rinsed in Milli-Q® ultrapure water. The next step was to submerge each tube in one to one nitric acid and then Milli-Q® ultrapure water was used to rinse off the acid. The tubes were handled with plastic forceps so no additional metal contamination took place.
    b. 100 mL of Milli-Q® ultrapure water was put through the 0.45 micrometer filter to ensure there is no residue on the filter before the run.
    c. The dissolved and total levels for Iron and Manganese were recorded.

9. The set up of the 0.45 micrometer filter that was used for the AA sampling was used to simulate filtration for the jar test. The filtered sample was collected in a sanitary flask. This water was used in the following steps of the procedure.
10. Before the test was run, pH and temperature tests were run and recorded.
11. After the experiment, samples for the dissolved and total manganese concentration were collected.
12. Samples for the dissolved and total iron concentration were collected.
13. Samples for total organic carbon were collected.
14. Samples for the UV 254 Absorbance test were collected.

3.6.2 Materials and Methods for Second Test with a pH Range of 8.0 to 8.8

1. The prefilter chlorine was off for 4 days.
2. 6 Liters of water were taken from the top of the filter on the day of the testing. The filter has been recently backwashed and does NOT contain prefilter chlorine in it.
3. There were 6 -1 Liter beakers filled to be put on the gang stirrer. A description of the six beakers follows:

Table 20. Elevated pH Prefilter Permanganate Dose Setup 2

	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
Actual pH	8.0	8.0	8.4	8.4	8.8	8.8
Sodium Permanganate Dose (mg/L)	0.1	0.1	0.1	0.1	0.1	0.1

4. 1 Molar NaOH was used to increase the pH to the desired level.
5. The stock solution of sodium permanganate is a 20% concentration and has a molecular weight of 142 gram/mole. To determine the molarity of the stock solution, the following equation was used.

$$\left(\frac{200{,}000\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 1.40845\ mol/L$$

To achieve a dilute solution of 1000 mg/L, the following equation was used.

$$\left(\frac{1000\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 0.0070422\ mol/L$$

Take 1 mL of stock solution and dilute it to a 1000 mg/L solution using the following equation.

$$M_1V_1 = M_2V_1$$

$$\left(1.40845\frac{mol}{L}\right) \times (0.005L) = \left(0.0070422\frac{mol}{L}\right) \times (\alpha\ L)$$

$$\alpha = 1\ L$$

Place 5 mL of stock solution into a 1L flask and fill the flask with deionized water. The result is working solution 1 and has a 1000 mg/L concentration.

To achieve a dilute solution of 100 mg/L, the following equation was used.

$$\left(\frac{100\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 7.0422 \times 10^{-4}\ mol/L$$

Take 100 mL of working solution 1 (1000 mg/L) and dilute it to a 100 mg/L solution using the following equation.

$$M_1V_1 = M_2V_1$$

$$\left(0.0070422\frac{mol}{L}\right) \times (0.100\ L) = \left(7.0422 \times 10^{-4}\frac{mol}{L}\right) \times (\beta\ L)$$

$$\beta = 1\ L$$

Place 100 mL of working solution 1 (1000 mg/L) into a 1 L flask and fill the flask with deionized water. The result is working solution 2 and has a 100 mg/L concentration. The second working solution is the solution that will be dosed into the jar to attain the correct concentration of sodium permanganate.

To attain a 0.1 mg/L concentration in the jar, 1 mL of working solution 2 was added to the jar. This is proved by the following equations.

$$\left(\frac{0.1\ mg\ NaMnO4}{L}\right) \times \left(\frac{1\ g}{1000\ mg}\right) \times \left(\frac{1\ mol\ NaMnO4}{142\ g}\right) = 7.0422 \times 10^{-7}\ mol/L$$

Take 1 mL of working solution 1 (1000 mg/L) and dilute it to a 1 mg/L solution using the following equation.

$$M_1V_1 = M_2V_1$$

$$\left(7.0422 \times 10^{-4}\frac{mol}{L}\right) \times (x\ L) = \left(7.0422 \times 10^{-7}\frac{mol}{L}\right) \times (1\ L)$$

$$x = 0.001\ L = 1\ mL$$

For all 6 jars, 1.0 mL of working solution 1 of sodium permanganate added to achieve a concentration of 0.10 mg/L sodium permanganate.

6. Next, the mixer on all six beakers at 15 RPM for 10 minutes The 15 RPM mixing replicated the gentle mixing in the flocculation basin.
7. Finally, the 6 beakers had no mixing for 30 minutes for quiescent settling.
8. A sample each beaker of was run on the Atomic Absorption instrument (AA) for Iron and Manganese.
    a. The testing tube for the AA was pre-rinsed in Milli-Q® ultrapure water. The next step was to submerge each tube in one to one nitric acid and then Milli-Q®

ultrapure water was used to rinse off the acid. The tubes were handled with plastic forceps so no additional metal contamination took place.

b. 100 mL of Milli-Q® ultrapure water was put through the 0.45 micrometer filter to ensure there is no residue on the filter before the run.

c. The dissolved and total levels for Iron and Manganese were recorded.

9. The set up of the 0.45 micrometer filter that was used for the AA sampling was used to simulate filtration for the jar test. The filtered sample was collected in a sanitary flask. This water was used in the following steps of the procedure.
10. Before the test was run, pH and temperature tests were run and recorded.
11. After the experiment, samples for the dissolved and total manganese concentration were collected.
12. Samples for the dissolved and total iron concentration were collected.
13. Samples for total organic carbon were collected.

3.6.3 Results and Discussion

Liquid sodium permanganate is an oxidant that works in the same way the more popular potassium permanganate works. Permanganate oxidizes the reduced (dissolved) manganese in the prefilter water. When the dissolved manganese is oxidized, it turns to manganese dioxide (MnO_2) which is a black powder capable of being removed in multimedia filtration.

A common problem with using permanganate to oxidize manganese is that if the dose is too low, the manganese will not be oxidized and if the dose is too high, then excessive manganese in the form of permanganate will pass through the filters. It is important to minimize

the dose while still attaining proper oxidation. The increase in pH allows permanganate to be a more effective oxidant at lower doses.

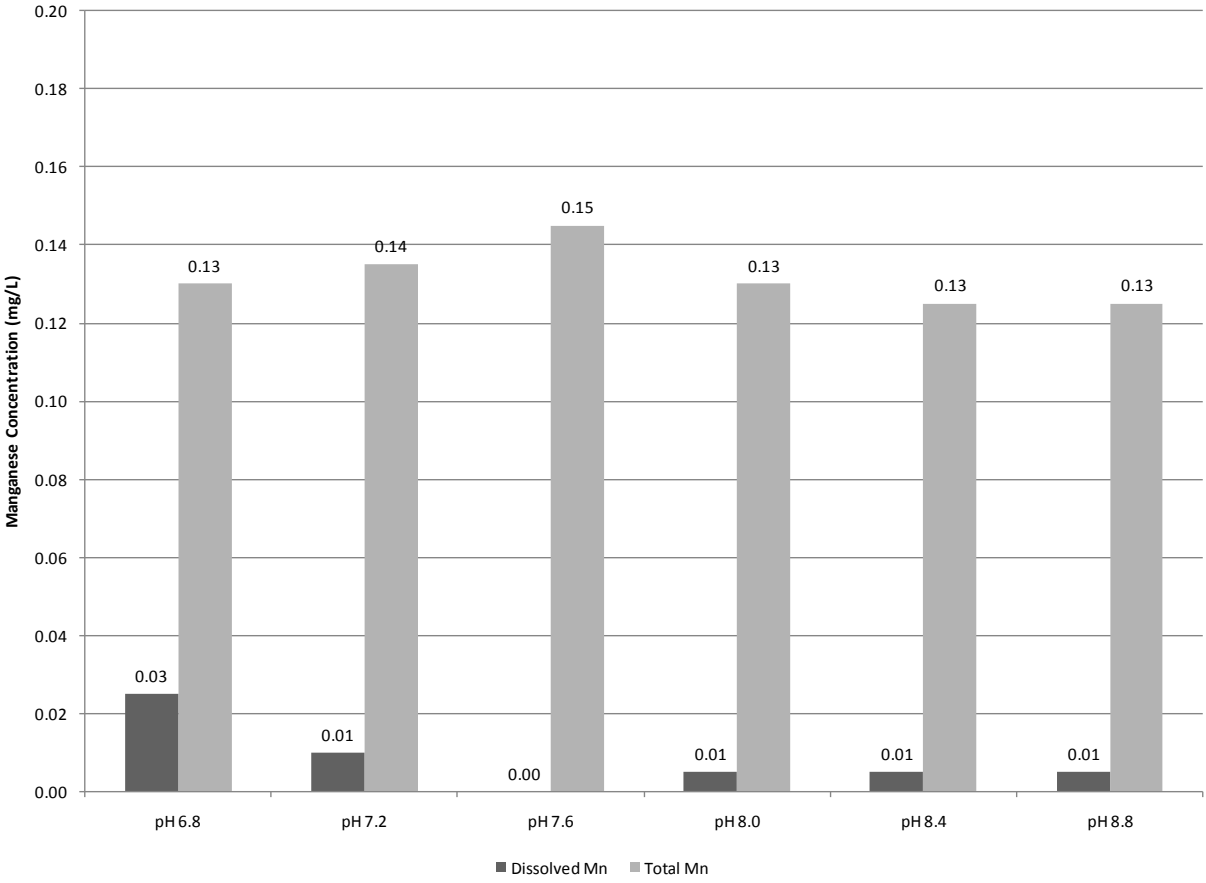

Figure 17. Elevated pH Prefilter Liquid Sodium Permanganate Dose 0.1 mg/L (Reduced Permanganate Dose) Bench-Scale Study

For the purposes of water treatment a manganese concentration after the filters of 0.01 mg/L or lower is undetectable by consumers and residents of the water distribution system. If the pH is increased to 7.2 above the filter using caustic soda and an innocuous amount of liquid sodium permanganate is dosed above the filters, manganese will be removed without increasing THM formation.

Figure 17 above shows that in water with a pH above 7.2, the 0.10 mg/L dose of sodium permanganate is adequate for manganese oxidation. For the intents and purposes of drinking

water utilities a concentration of 0.01 mg/L for manganese is undetectable by customers. The entire reduced dose prefilter permanganate bench-scale tests at varying pH data is found in Appendix D.2.

4.0 PLANT-SCALE EXPERIMENTS

4.1 PREFILTER CHLORINATION THM STUDY

It is important to fully understand what the effects of prefilter chlorination are on the formation of trihalomethanes. Currently the prefilter chlorination is used to control the level of manganese removal. It is still unknown how much the prefilter chlorination adds to the disinfection byproduct production. This plant-scale test will provide some insight on the effects of prefilter chlorination in terms of THM formation potential.

4.1.1 Materials and Methods

There is an 8 hour travel time for a pocket of water to travel from the bottom of the filter to the outlet house in the clearwell at PWSA's water treatment plant. Samples were taken at 7:30am from the bottom of a recently backwashed filter. Then later that same day at 3:30pm, 8 hours later, samples were taken from the outlet house in the clear well. The time lapse based on a previous tracer study by PWSA ensures that both samples of the day were taken from the same "pocket of water" [States, 2009].

The following were tested in duplicate every time a sample was taken:

1. pH
2. Temperature

3. Turbidity
4. Free chlorine
5. Total chlorine
6. TOC
7. UV 254 absorbance
8. THM
9. THMFP7
10. THMFP14 (was completed in later testing)

This procedure was repeated eight times to provide duplicity to the study. In later tests, prefilter water was analyzed as well as THMFP14 in the postfilter and clearwell water. The first time that this test was performed the prefilter chlorine was turned off in the beginning of the week and the plant became steady state without prefilter chlorine on. Subsequent times this test was performed, the plant was already in steady state with the prefilter chlorine on, then it was turned off and once there was no residual chlorine on the filters the second set of samples were taken. The reason behind the change in testing protocol was to accommodate PWSA turning on and off the plant prefilter chlorination.

Table 21. Prefilter Chlorination Plant-Scale Study Dates and Comments

Trial 1	March 2009	PFC **OFF** then PFC **ON**
Trial 2	March 2009	PFC **OFF** then PFC **ON**
Trial 3	March 2009	PFC On then PFC Off
Trial 4	March 2009	PFC **OFF** then PFC **ON**
Trial 5	April 2009	PFC On then PFC Off
Trial 6	April 2009	PFC On then PFC Off
Trial 7	June 2009	PFC On then PFC Off
Trial 8	June 2009	PFC On then PFC Off

Above Table 21 shows that trials 1, 2 and 4 had the prefilter chlorine off then was turned back on. Trial 4 allowed for adequate time (3 days) for the plant to reach steady state. Additional data for the Prefilter Chlorination THM Study is found in Appendix E.

4.1.2 Results and Discussion

The following plant-scale experiment was conducted to determine the actual effect of prefilter chlorination in terms of THM formation potential. There were four tests completed with 4 runs per test, and each test contained between 32 and 48 data measurements. The only way to present trends of the data is in graphs. The complete analysis data is located in the Appendix E.

4.1.2.1 Total Organic Carbon Results and Discussion

Total organic carbon (TOC) and UV 254 absorbance are both measures of the concentrations of organic matter present in the water. Organic matter in water usually contains many rings and functional groups. If free chlorine is present it will attack and replace certain hydrogen molecules with halogens. If these newly chlorinated functional groups break their bonds to the normal organic matter, small chlorinated organics are formed such as haloacetic acid and trihalomethanes. Both TOC and UV 254 were analyzed during all of the runs.

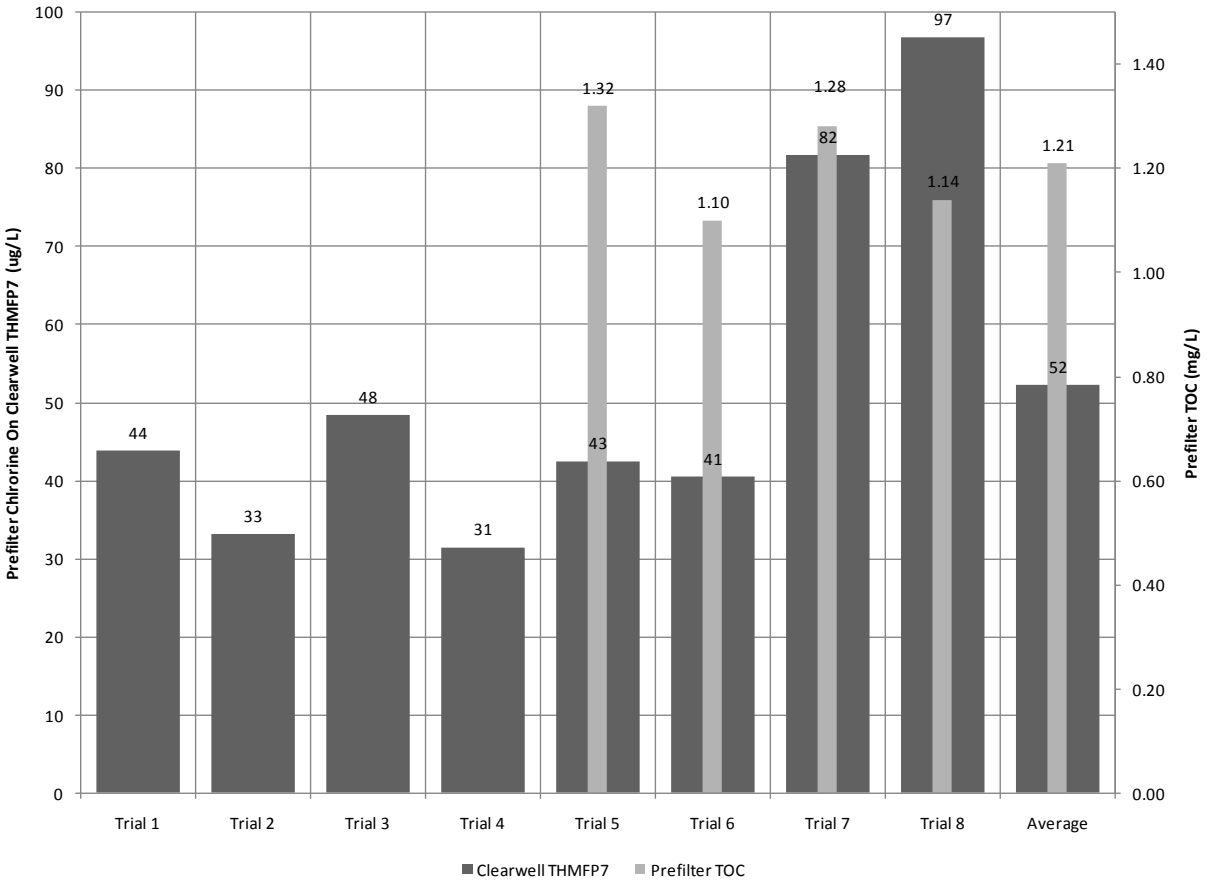

Figure 18. Prefilter Chlorine On: Prefilter TOC Levels and the Effects on Clearwell THMFP7 Plant-Scale Study

It should be noted that prefilter wet chemistry was not completed for the first 4 trials, it was later in the research that it was decided the data would be beneficial. Logic suggests that with an increase of prefilter TOC concentration there should be an increase in the THM formed in the clearwell. However, Figure 18 does not support this hypothesis. However, the results do not disprove the hypothesis either, the results are simply inconclusive. The major point is to see if prefilter chlorination affects the trihalomethane potential in the clearwell after 7 days. The average THMFP7 in the clearwell when prefilter chlorination was in place was 52 μg/L, this is shown in Figure 18. The average THMFP7 in the clearwell when prefilter chlorination was off was 49 μg/L, this is shown if Figure 19. Figure 19 follows the general accepted trend that as

total organic carbon increases so does the THM formation potential. However it should be noted that the margin of error of the gas chromatography-mass spectrometer is 15 to 20% and the results are inconclusive.

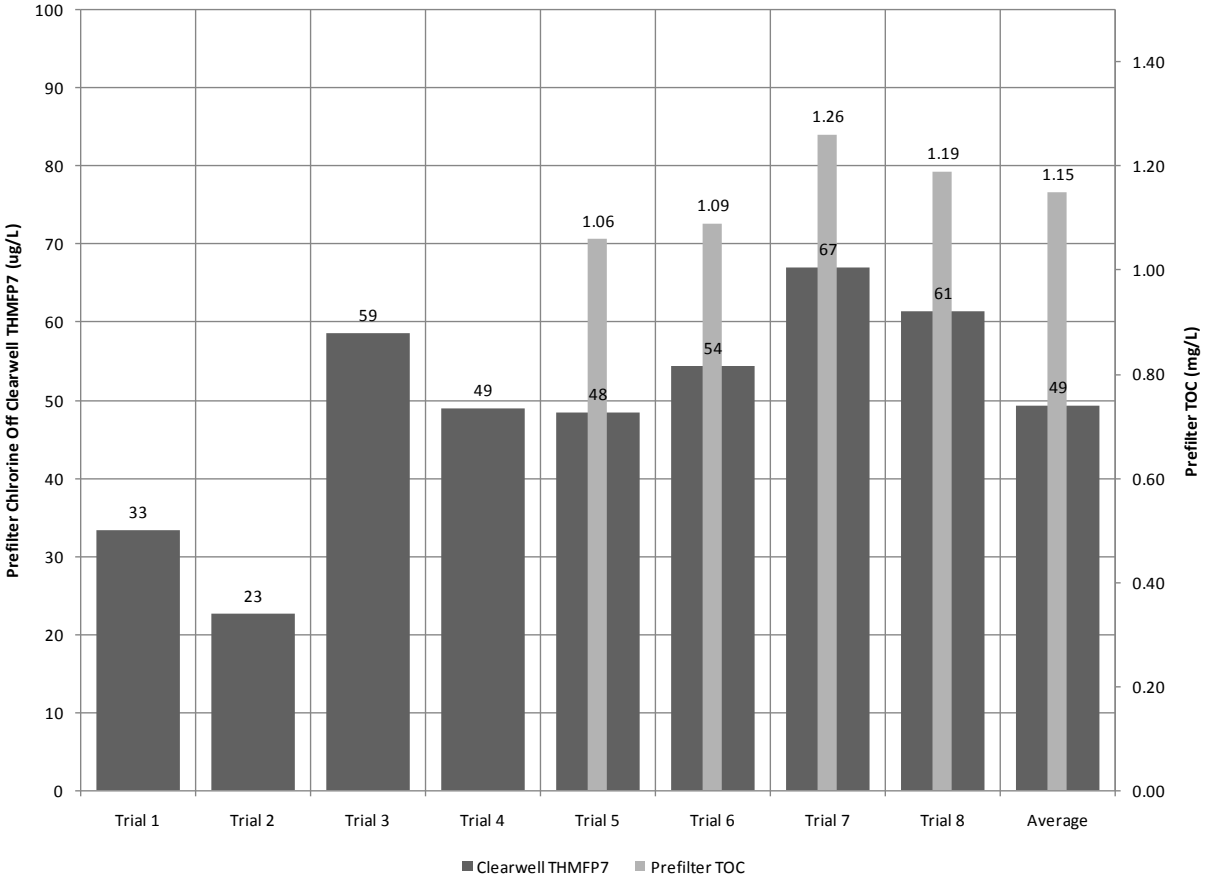

Figure 19. Prefilter Chlorine Off: Prefilter TOC Levels and the Effects on Clearwell THMFP7 Plant-Scale Study

4.1.2.2 UV 254 Absorbance Results and Discussion

Both TOC and UV 254 absorbance measure organic matter in water. The concentration of organic matter in water correlates with the concentration of disinfection byproducts after chlorination. UV 254 absorbance can provide inexpensive and meaningful prescriptive guidance for disinfection processes especially for daily operating purposes. A more accurate and accepted

portrayal of organic matter concentration is achieved by measuring total organic carbon. UV 254 absorbance can be used in addition to TOC testing to provide additional data on organic matter concentration and removal.

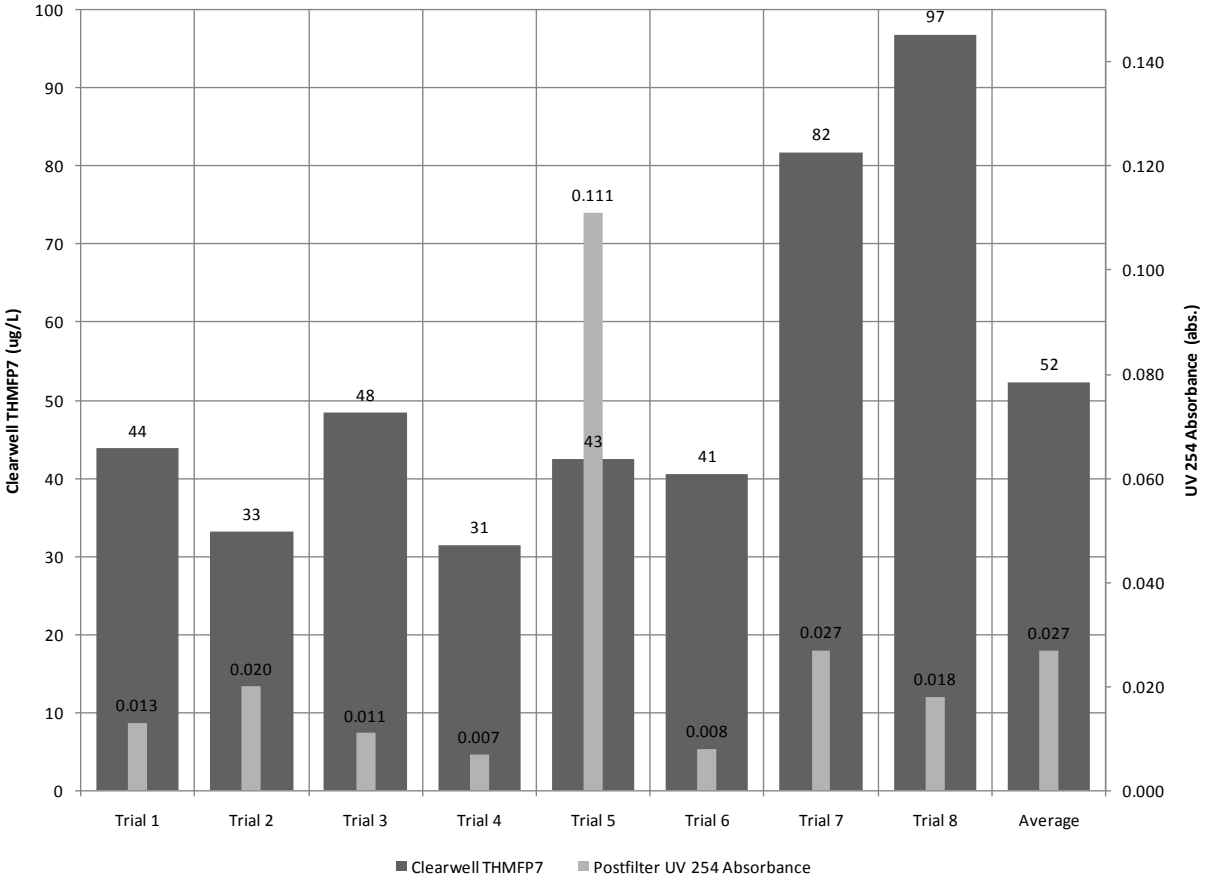

Figure 20. Prefilter Chlorine On: Postfilter UV 254 Absorbance and the Effects on Clearwell THMFP7 Plant-Scale Study

In Figures 18 and 20, the UV 254 absorbance trend follows the TOC trend. When the prefilter chlorine is on and when the UV 254 absorbance is higher, the resulting THM formation potential in the clearwell is greater. Similarly to the TOC graphs in the previous section, the level of TOC, or in this case UV 254 absorbance, does not directly coincide with levels of THM formation.

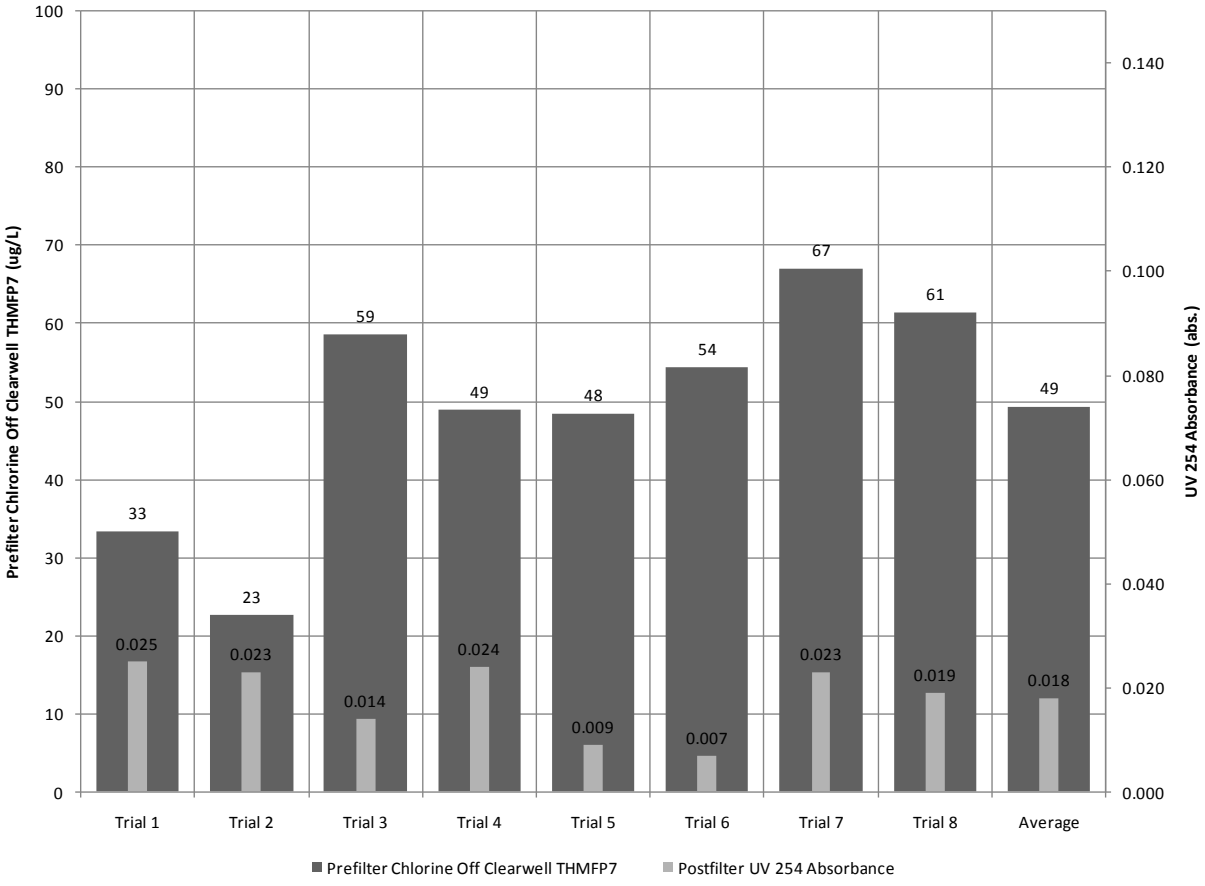

Figure 21. Prefilter Chlorine Off: Post filter UV 254 Absorbance and the Effects on Clearwell THMFP7 Plant Scale- Study

There are still no definitive conclusions from this study, either the instrument error is too great or there is no measurable effect of prefilter chlorination at the current PWSA dosage. PWSA strives to minimize the chlorine dosage both above the filters and in the clearwell. If the dose were increased to 5 or 10 mg/L there would be significant THM formation, well beyond the EPA limits. Proper management of the utility and chlorine dosage results in the minimization of disinfection byproducts [States, 2009].

4.1.2.3 Chlorine Dose Results and Discussion

In addition to the concentration of organic matter present in the water, the chlorine dose also factors in to the trihalomethane formation potential. Below in Figure 22, the total chlorine concentration found in the clearwell is on the x axis and the clearwell THMFP7 is represented on the y axis. As hypothesized, there should be a positive sloping trend line for both data sets. As shown below, there is no trend present.

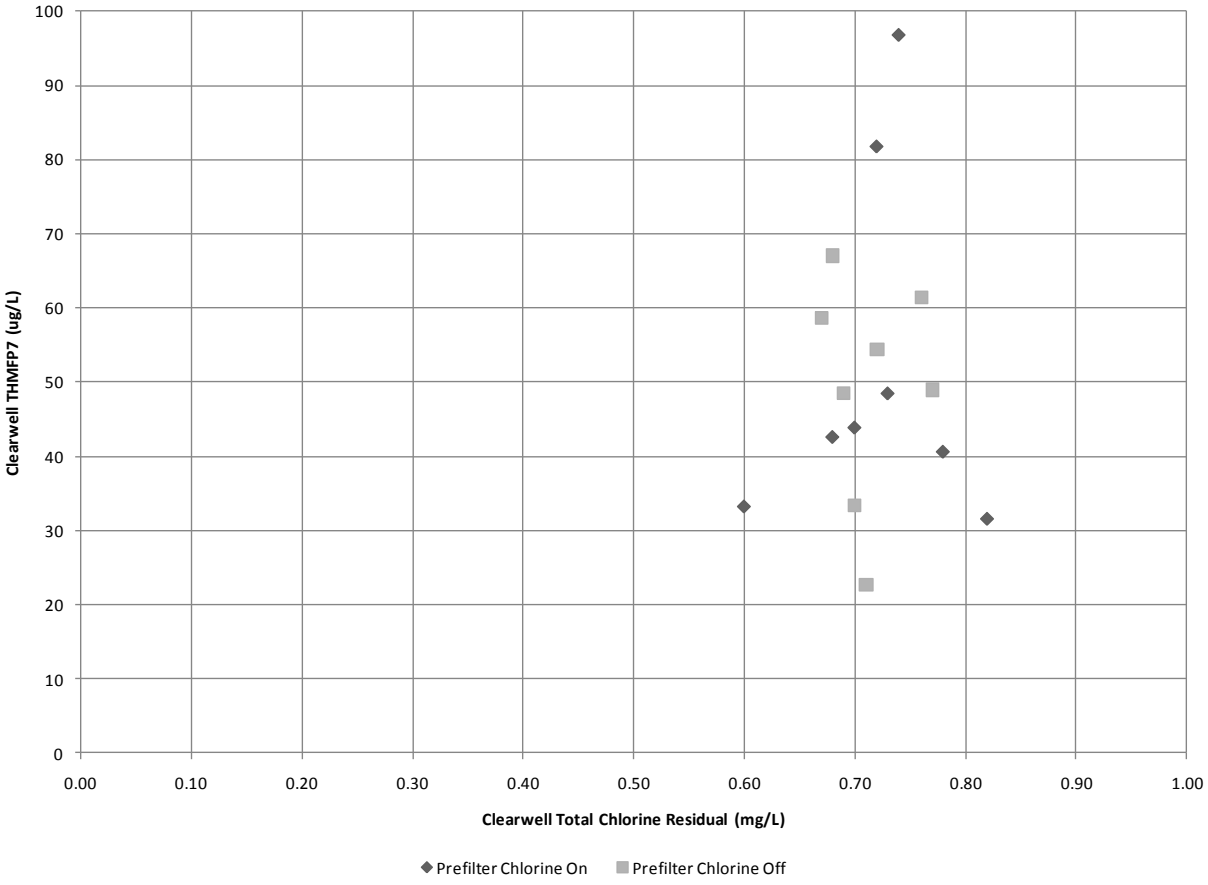

Figure 22. Clearwell Total Chlorine Residual and the Effects on Clearwell THMFP7 Plant-Scale Study

4.1.3 Summary and Conclusions

Figure 23 below summarizes the prefilter chlorination THM study, it shows eight sets of trials one that has been prefilter chlorinated and one that has not been. The results show that prefilter chlorination creates more trihalomethanes in the clearwell after seven days. However, the data shown below is too close and within the error margin of the instrument to be completely conclusive.

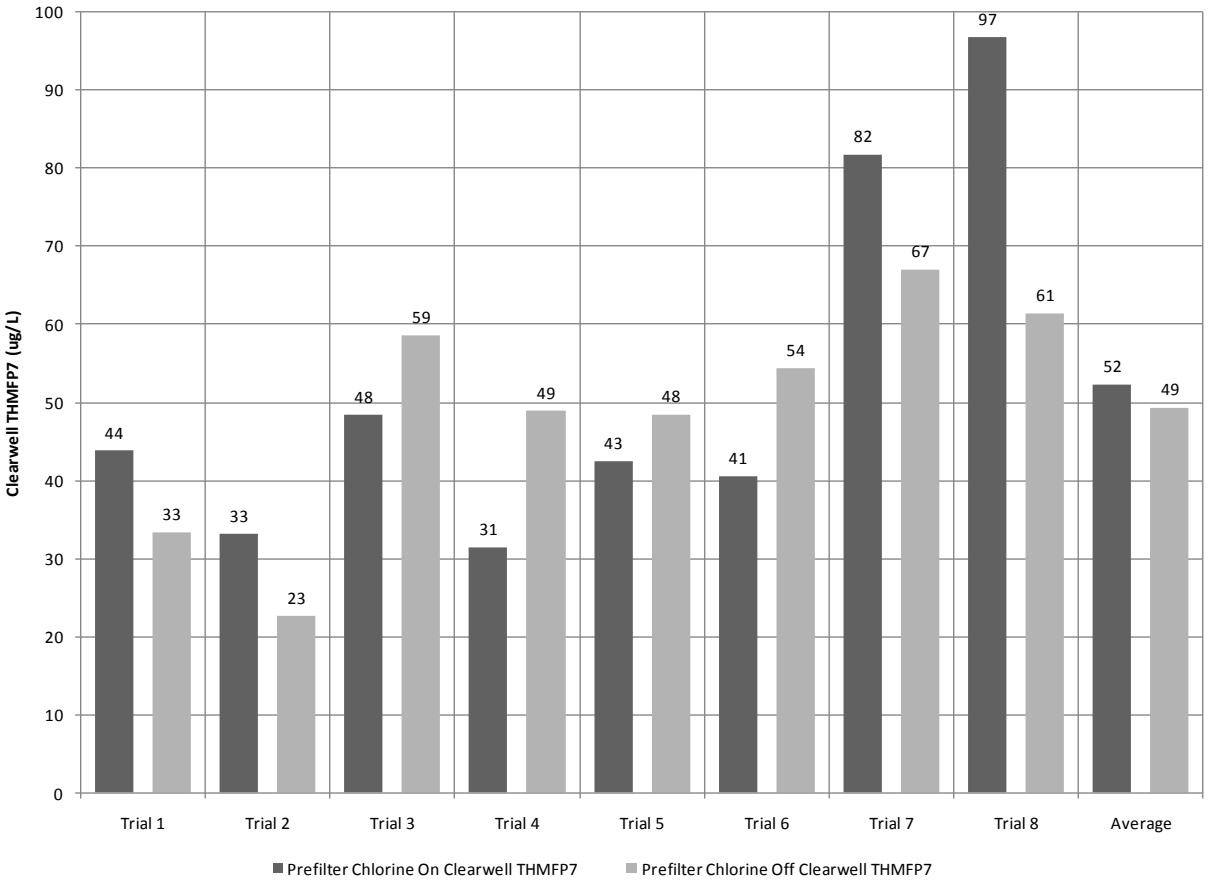

Figure 23. Prefilter Chlorination and the Effects on Clearwell THMFP7 Plant-Scale Study

Below Table 22 shows that trials 1, 2 and 4 had the prefilter chlorine off then was turned back on. Trial 4 allowed for adequate time (3 days) for the plant to reach steady state. Additional data for the Prefilter Chlorination THM Study is found in Appendix E.

Table 22. Prefilter Chlorination Plant-Scale Study Dates and Comments

Trial 1	March 2009	PFC **OFF** then PFC **ON**
Trial 2	March 2009	PFC **OFF** then PFC **ON**
Trial 3	March 2009	PFC On then PFC Off
Trial 4	March 2009	PFC **OFF** then PFC **ON**
Trial 5	April 2009	PFC On then PFC Off
Trial 6	April 2009	PFC On then PFC Off
Trial 7	June 2009	PFC On then PFC Off
Trial 8	June 2009	PFC On then PFC Off

At the current levels of prefilter chlorination, there is no significant increase in THM formation potential. The best way to minimize the disinfection byproducts is to remove disinfection byproduct precursor, namely TOC and UV 254 absorbance. In section 4.3, disinfection byproduct precursors are addressed more completely.

4.2 CHLORINE SPIKE EXPERIMENTS

Although the prefilter chlorination THM study was inconclusive because of the chlorine residual based disinfection, a more direct experiment was devised to eliminate a number of the unknowns inherent with plant sampling. The premise of this experiment was to find exactly what the effect of prefilter chlorination was. Multiple tests have proven that there was a TOC and UV 254 absorbance reduction from the top of the filter to the bottom of the filter. Theory suggests that

chlorinating water with elevated amounts of disinfection byproduct precursor such as TOC and UV 254 absorbent materials will increase the THM formation potential.

The chlorine spike experiment takes samples from the plant above and below the filter. It is necessary for the prefilter chlorine to be off for the plant. Each sample, collected in duplicate, is injected with a dose of chlorine of a specified amount. The chlorine residual is tested and the injected samples incubate in the water bath for seven days. After which, the samples are quelched with thiosulfate to prevent any more THM formation. Each sample is run on the gas chromatography mass spectrometer and analyzed for total trihalomethanes.

4.2.1 Materials and Methods

The prefilter chlorine is turned off in the plant for at least two days. The two day period allows the chlorine to be flushed from the filters and not interfere with the study. Samples above and below the filters are gathered in 60 mL head space free vials.

Multiple runs of this experiment were completed. Each run used a different dose of chlorine, the first used 0.5 mg/L to simulate the 0.3 to 0.5 mg/L PWSA prefilter chlorine dose. The second used 1.0 mg/L and to achieve more dramatic results the last test used a chlorine dose of 2.0 mg/L. Calculations are made to determine the dilution and volume injected of chlorine to the 60 mL vial to create a 0.5, 1.0 or a 2.0 mg/L dose. The dosing and dilution depends on the strength of the stock solution which can vary between 10% and 16%. A series of checks were put into place to test the stock solution and ensure the correct dosage in each 60 mL vial.

Each sample, collected in duplicate, is injected with a dose of chlorine of a specified amount to create a 0.50, 1.0 or a 2.0 mg/L dose. The chlorine spike experiment bench-scale study using plant water with the 0.5 mg/L dose took place on June 3 and June 4, 2009. The

chlorine spike experiment with the 1.0 mg/L chlorine dose took place on June 18 and June 19, 2009. The chlorine spike experiment with the 2.0 mg/L dose took place on July 23 and July 24, 2009. The total chlorine residual is tested and recorded. The 40 mL that is left of the sample is transferred to a 40 mL head space free vial. The vials are put in a water bath at 26.7 °C (80°F) for seven days. After which, the samples are quelched with thiosulfate to prevent any more THM formation. Each sample is run on the gas chromatography mass spectrometer and analyzed for total trihalomethanes.

4.2.2 Results and Discussion

In the prefilter chlorination THM study, there were simply too many uncontrollable variables. There were seasonal changes in the raw water, there was maintenance being performed on the flocculation basins and rapid mix systems, there were times of heavy metal concentrations in the prefilter water and there were times of above average organic carbon loading on the filters.

In order to minimize the number of variables and set up more controls the chlorine spike experiments were devised. Water is sampled from both the top and bottom of the same filter two hours apart. Both samples are injected with the same dose of chlorine, be it 0.5, 1.0 or 2.0 mg/L. The chlorinated samples are incubated in the water bath at 26.7 °C (80 °F) for seven days then quelched with thiosulfate and run on the gas chromatography mass spectrometer for total trihalomethanes. The total residual chlorine is also measured to determine how much chlorine is used in the seven days.

The chlorine spike experiment bench-scale study using plant water with the 0.5 mg/L dose took place on June 3 and June 4, 2009. The chlorine spike experiment with the 1.0 mg/L

chlorine dose took place on June 18 and June 19, 2009. The chlorine spike experiment with the 2.0 mg/L dose took place on July 23 and July 24, 2009.

Figure 24 below compares the THM formation potential after seven days for water that has been chlorinated above and below the filters. There is a 20% instrument error associated with the gas chromatography mass spectrometer so error bars were included in the bar graphs. Figure 24 shows that on average postfilter chlorination creates more disinfection byproducts when dose at 0.5 mg/L. However, it is very important to note that this test could be inconclusive because of the error associated with the instrument. Both prefilter and postfilter results are close enough to fall within the error margin. Figure 25 shows the results after the 60 mL vials were dosed with 1.0 mg/L of chlorine.

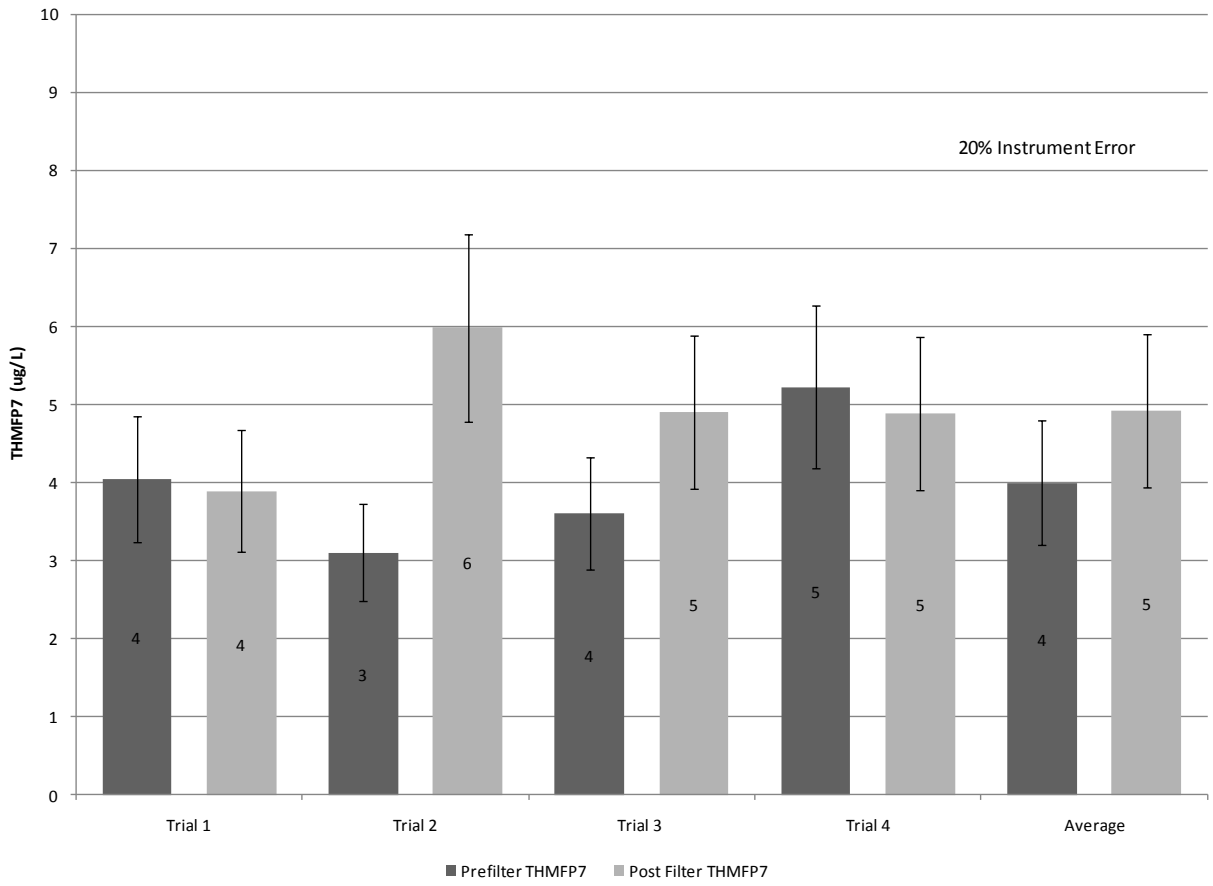

Figure 24. Chlorine Spike 0.5 mg/L Dose Comparison of Prefilter and Postfilter Chlorination Bench-Scale Study Using Plant Water

Figure 25 below shows that on average prefilter chlorination created more disinfection byproducts when dosed at 1.0 mg/L. The greater THM concentration was expected and supports the hypothesis from earlier. It should also be noted that the variance between prefilter and postfilter THM formation is beyond the error margin. However, it is very important to note that this test could be inconclusive because of the error associated with the instrument. Both prefilter and postfilter results are close enough to fall within the error margin. Figure 26 shows the results after the 60 mL vials were dosed with 2.0 mg/L of chlorine.

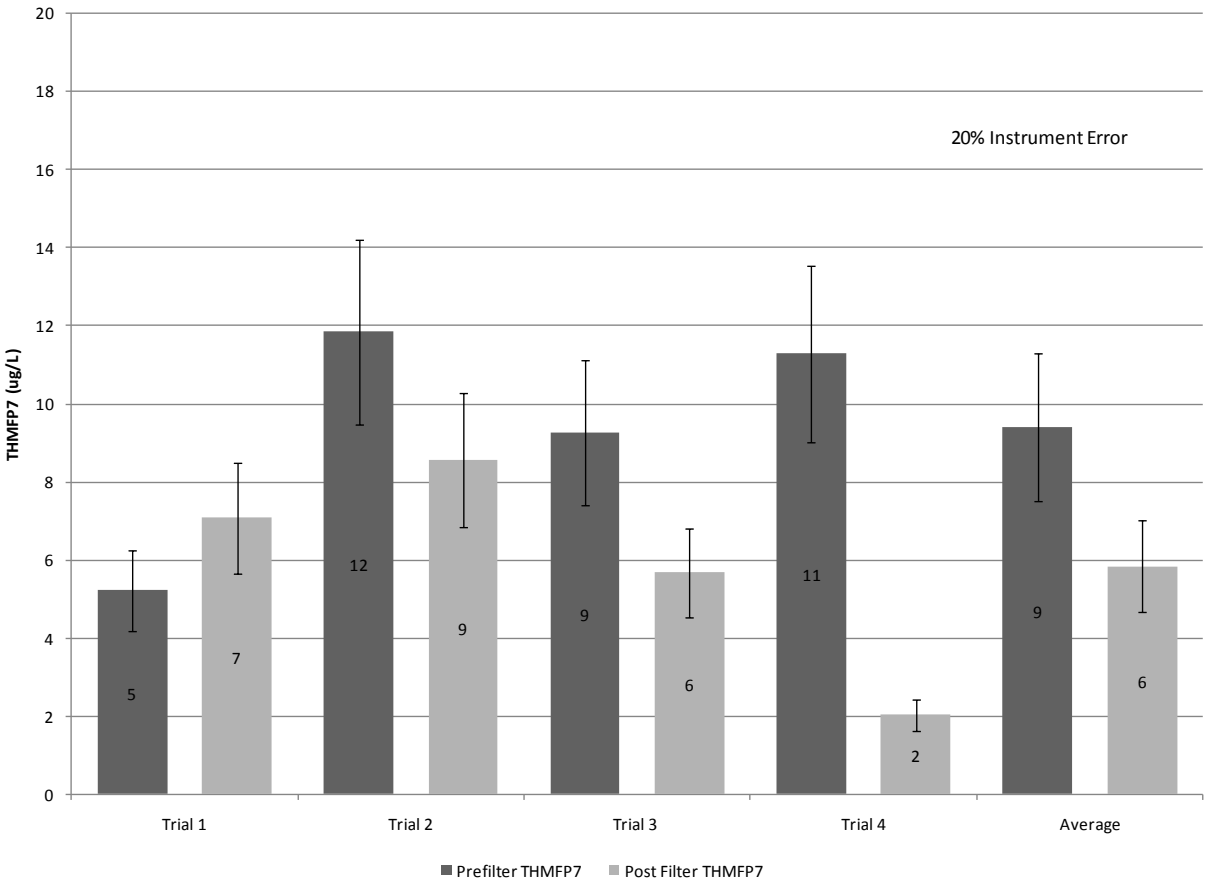

Figure 25. Chlorine Spike 1.0 mg/L Dose Comparison of Prefilter and Postfilter Chlorination Bench-Scale Study Using Plant Water

Figure 26 below shows the results from 2.0 mg/L dosing of chlorine. It should be noted that PWSA does not dose prefilter chlorination or even clearwell chlorination at this high of a concentration. The 2.0 mg/L concentration was chosen for this experiment to attain more dramatic more conclusive results. Theoretically organic matter should be removed by the filters and there should be more organic matter prefilter than postfilter. When the chlorine dose is increased to such a dramatic level, the THM formation potential after seven days should much higher in the prefilter water compared to the postfilter water.

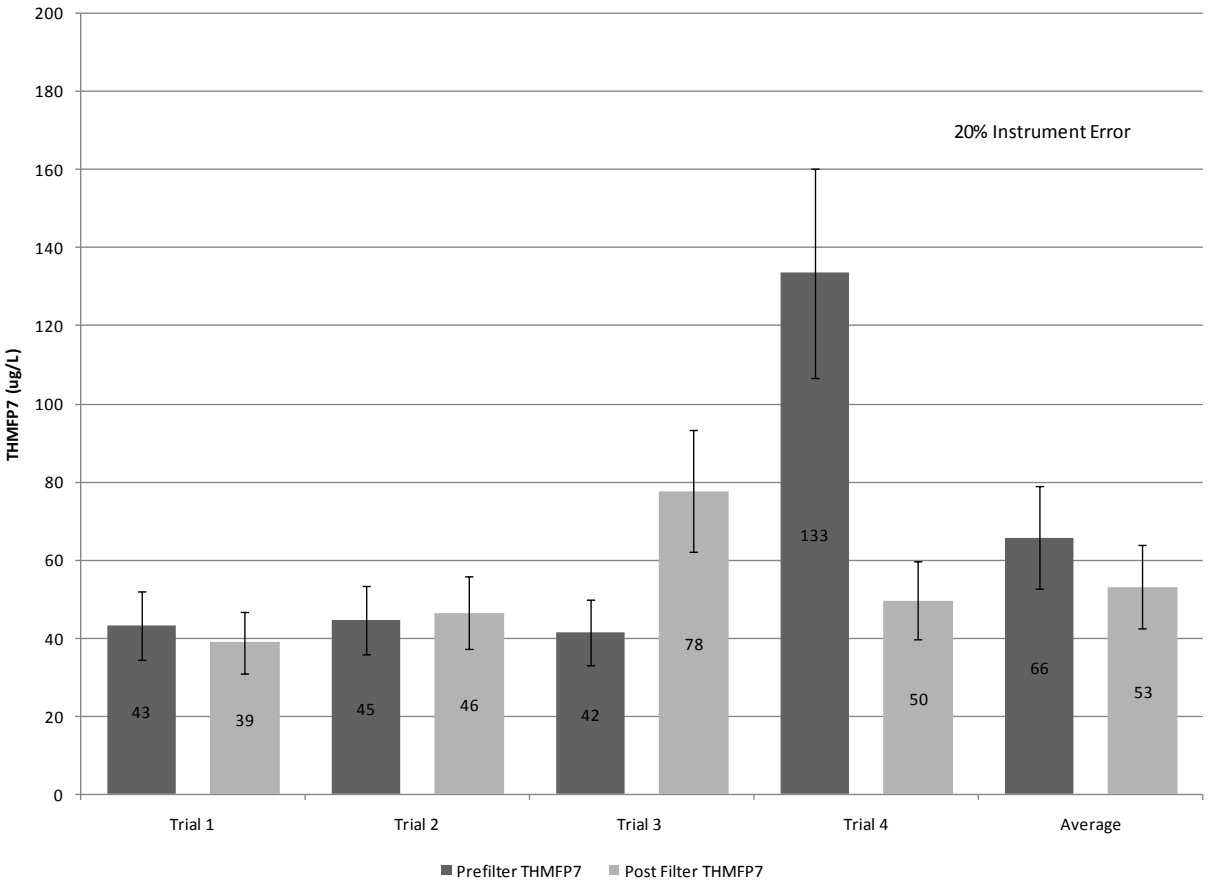

Figure 26. Chlorine Spike 2.0 mg/L Dose Comparison of Prefilter and Postfilter Chlorination Bench-Scale Study Using Plant Water

Due to some instrument error in the 2.0 mg/L chlorine spike experiment (Internal standards of the gas chromatography mass spectrometer were reading abnormally low) tests 3 and 4 should be omitted from the analysis. Test 1 and Test 2 are both close in number and within each other's margin of error. A possible explanation for this is that when such a great amount of chlorine added (four times the normal amount), the difference in organic material prefilter and postfilter does not matter because it is small in comparison to the chlorine dose. In further experiments, a TOC profile of the entire plant including every unit process is created. The results from that experiment show that most of the organic carbon removal is in the flume right after the rapid mix. The filters do not remove much in comparison to the flume.

Figure 27 is a graph of data from the 0.5 mg/L dose experiment. It portrays the chlorine residual after seven days in the water bath. Figure 23 shows that even though the dose was 0.5 mg/L the residual of total chlorine was 0.32 mg/L. The 0.32 mg/L residual chlorine means that an average of 0.18 mg/L of chlorine was consumed which is 36% of the total dosage.

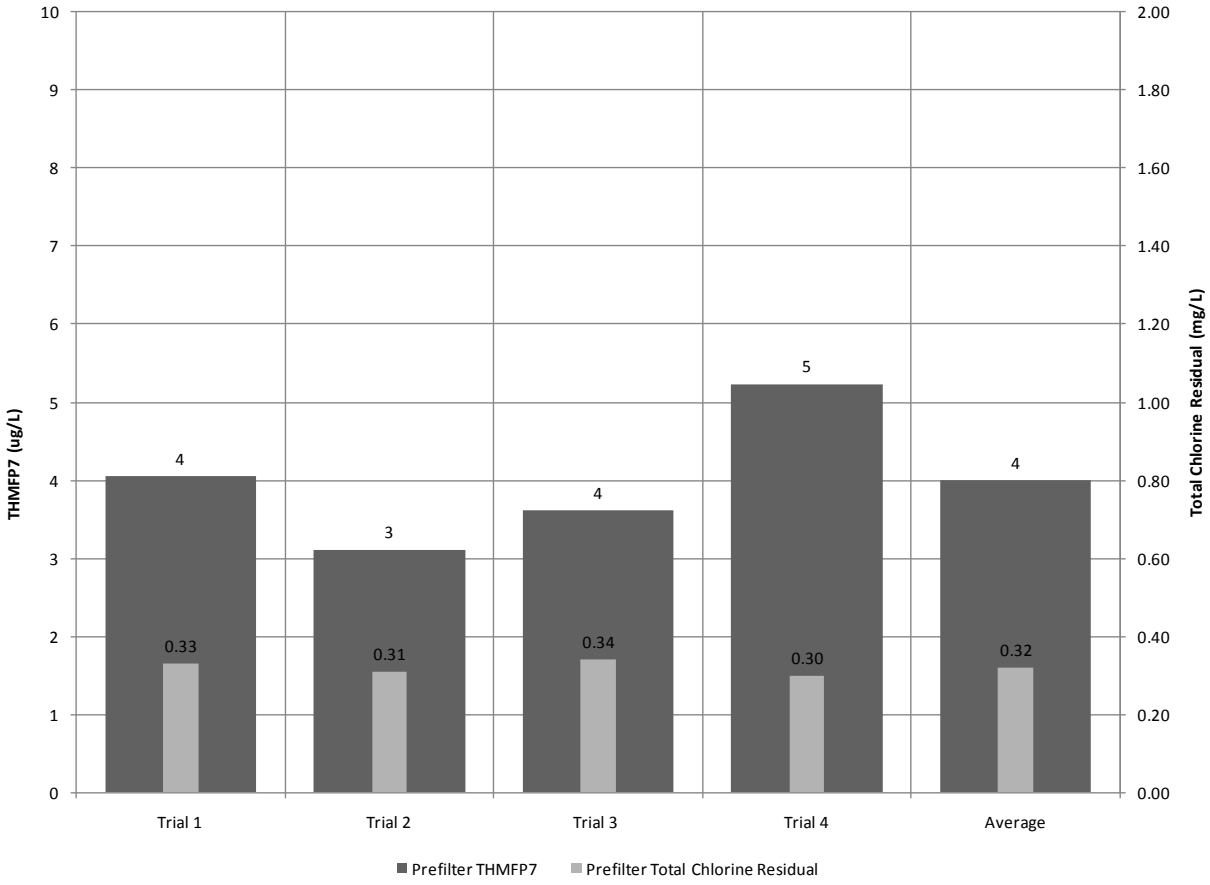

Figure 27. Chlorine Spike 0.5 mg/L Dose: Total Residual Chlorine and THMFP7 for Prefilter Chlorination Bench-Scale Study Using Plant Water

Figure 28 shows the postfilter data from the 0.5 mg/L experiment. Similarly to the prefilter experiment at 0.5 mg/L, the average total chlorine residual is 0.29 mg/L. Chlorine is consumed by organics, metals and by sunlight and heat. Because the vials are sealed with zero head space, there are no losses to heat and light.

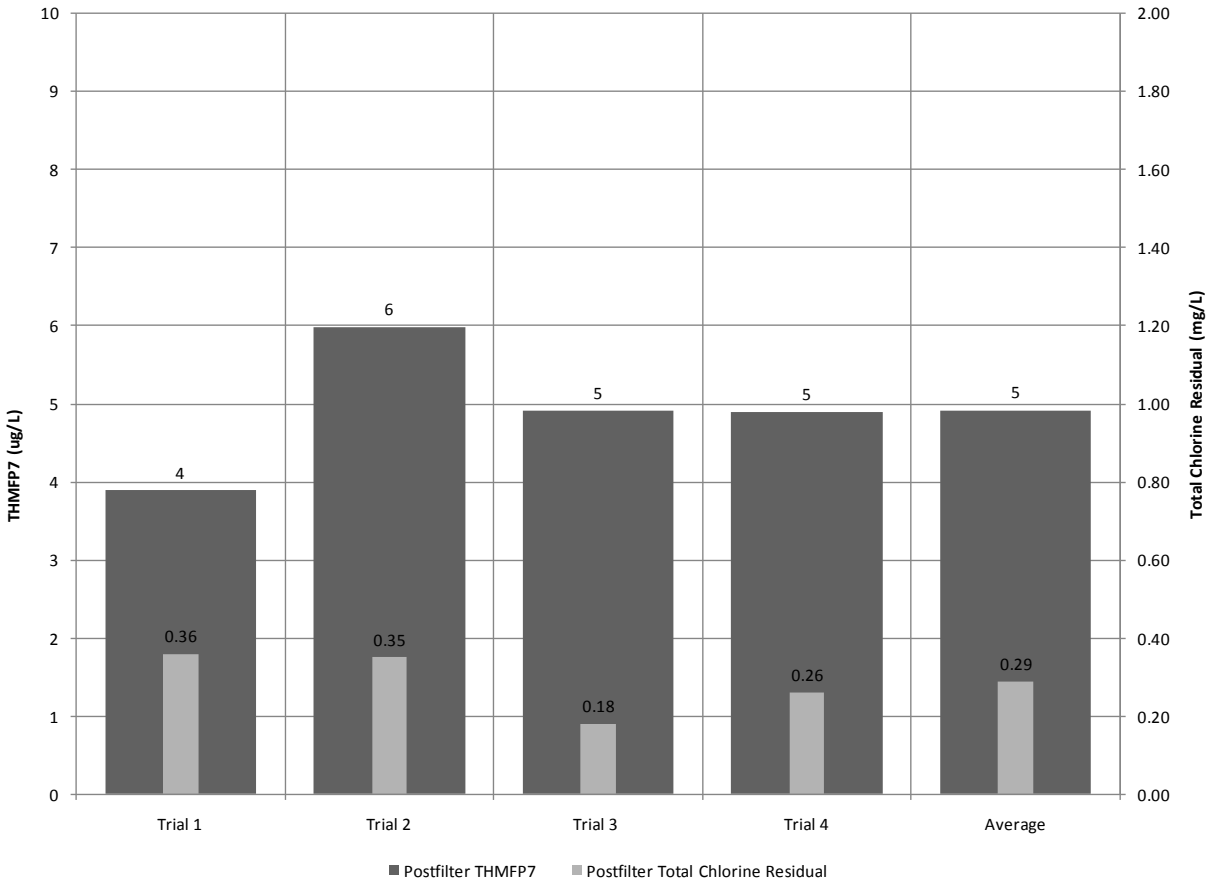

Figure 28. Chlorine Spike 0.5 mg/L Dose: Total Residual Chlorine and THMFP7 for Postfilter Chlorination Bench-Scale Study Using Plant Water

Figure 29 shows data from the prefilter chlorination 1.0 mg/L dose experiment. The average usage of chlorine during prefilter chlorination was 0.20 mg/L which is 20% of the original dosage. The prefilter usage for 1.0 mg/L is less than the prefilter chlorine usage of 0.5 mg/L.

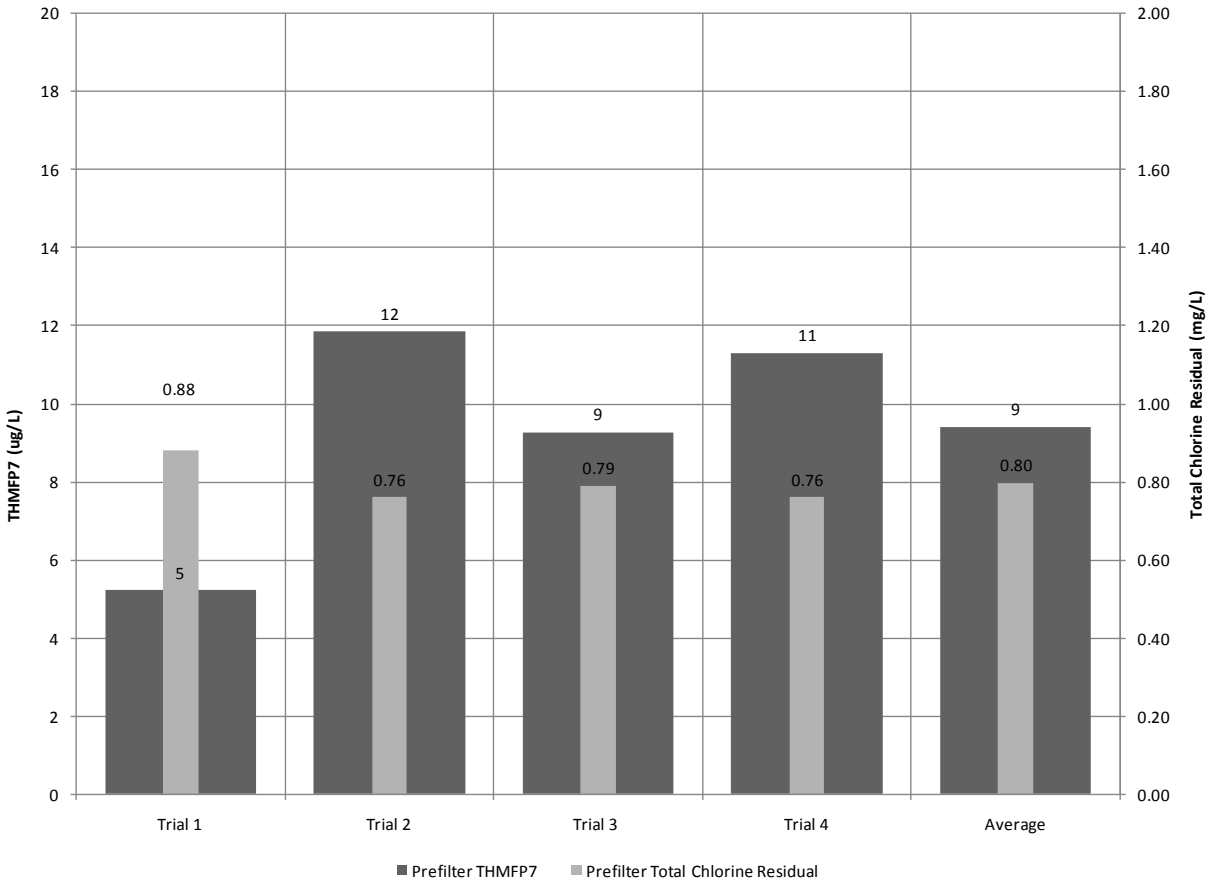

Figure 29. Chlorine Spike 1.0 mg/L Dose: Total Residual Chlorine and THMFP7 for Prefilter Chlorination Bench-Scale Study Using Plant Water

Below in figure 30, the postfilter chlorination 1.0 mg/L dose experiment. The average usage of chlorine spike experiment. Another point supporting the hypothesis that prefilter chlorination should have a larger demand on the chlorine is that there was on average a 9 µg/L concentration of THMs formed and on water that was postfilter chlorinated there was an average of 6 µg/L concentration of THMs formed.

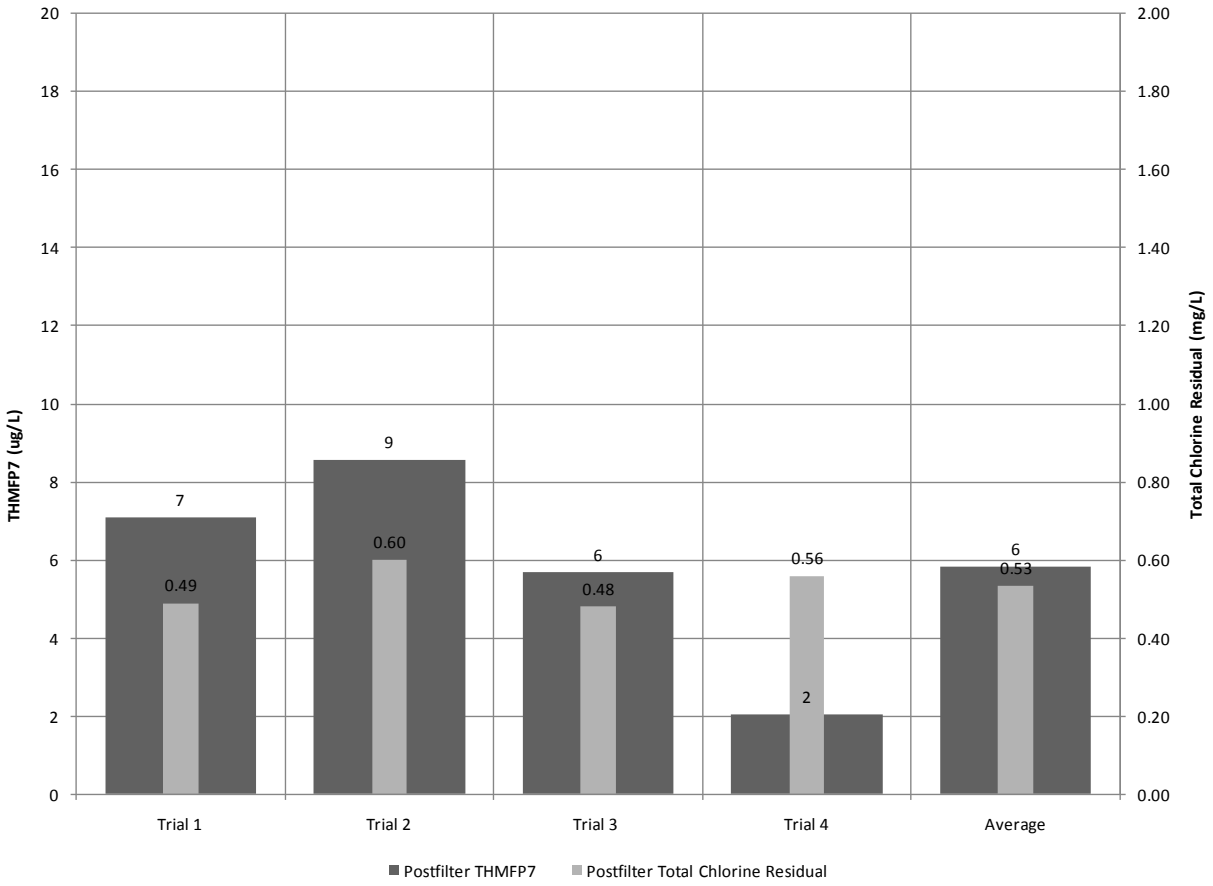

Figure 30. Chlorine Spike 1.0 mg/L Dose: Total Residual Chlorine and THMFP7 for Postfilter Chlorination Bench-Scale Study Using Plant Water

Figure 31 shows data from the prefilter chlorination 2.0 mg/L dose experiment. The average usage of chlorine during prefilter chlorination was 1.96 mg/L which is 98% of the original dosage. The prefilter usage for 2.0 mg/L is greater than the postfilter chlorine usage of 2.0 mg/L by 1%. The trihalomethane formation potential for both the prefilter and post filter were the highest out of all the experiments. The increase in THMs is most likely due to the doubling or quadrupling of the chlorine dose from the 0.5 and 1.0 mg/L experiments.

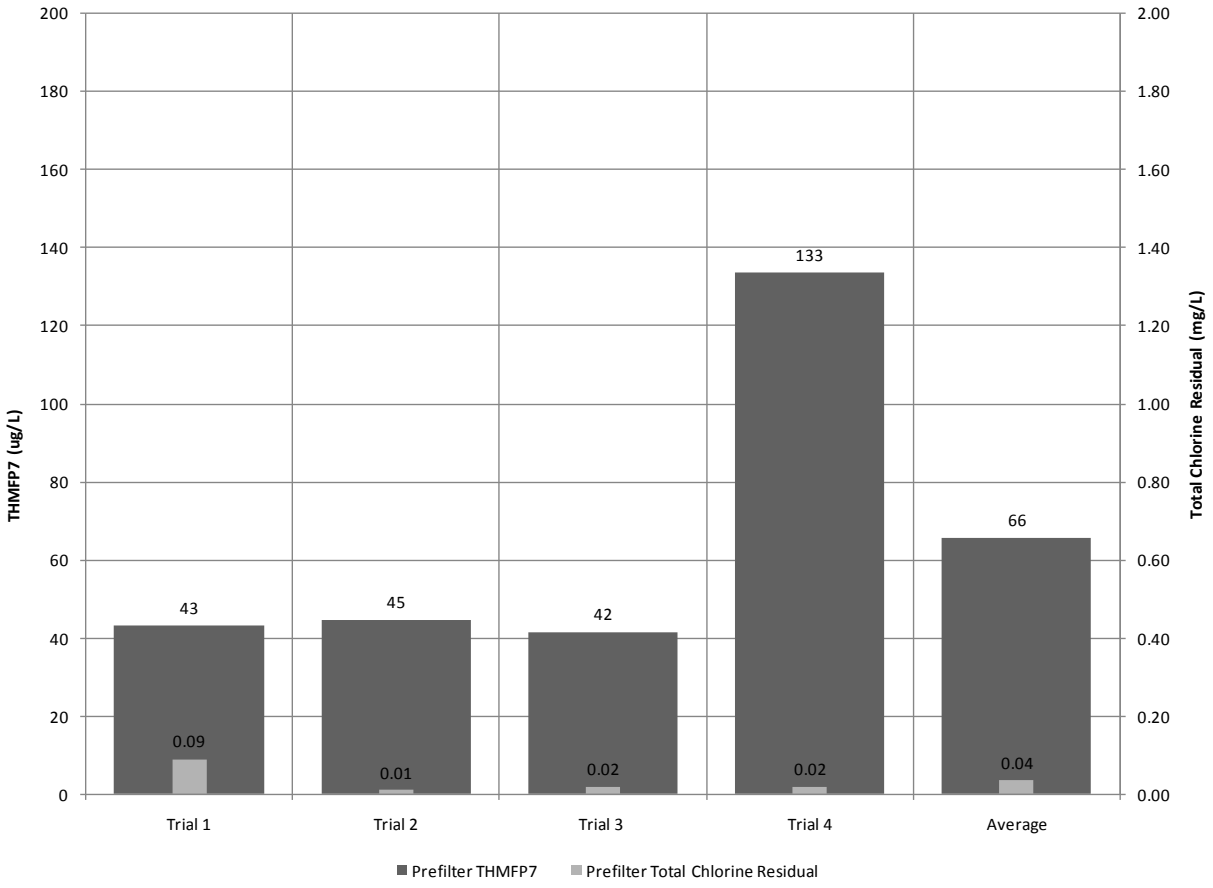

Figure 31. Chlorine Spike 2.0 mg/L Dose: Total Residual Chlorine and THMFP7 for Prefilter Chlorination Bench-Scale Study Using Plant Water

Below figure 32 shows the postfilter trihalomethane formation potential after seven days to be on average 13 µg/L less than the prefilter trihalomethane formation potential. The 13 µg/L difference still falls within the 15 to 20% range of instrument error. Although another test with a higher chlorine dose might increase the gap between pre and postfilter chlorination. The PWSA free and total chlorine sampler has a maximum reading of 2.2 mg/L. Also any prefilter chlorination study larger than a 1.0 mg/L dose is beyond normal operating circumstances for PWSA's prefilter chlorination in their water treatment plant.

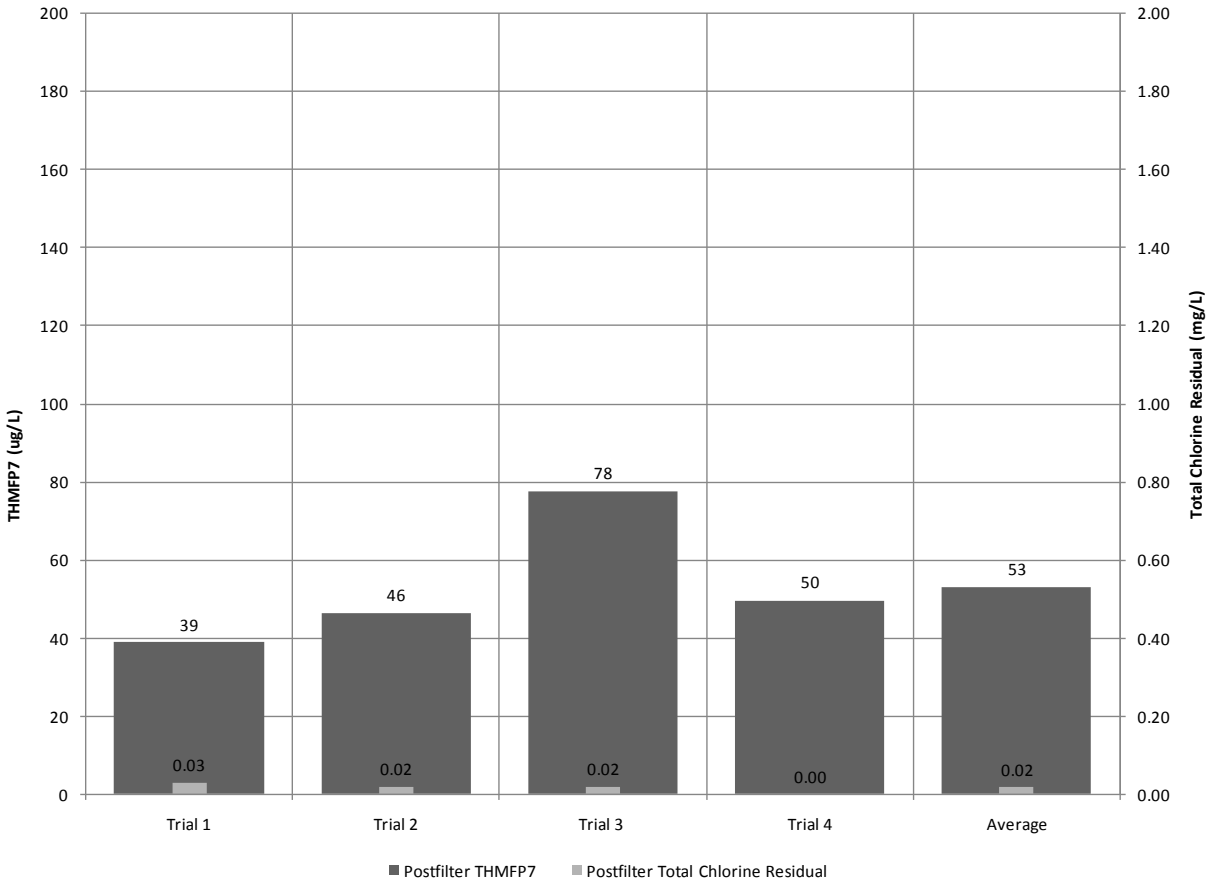

Figure 32. Chlorine Spike 2.0 mg/L Dose: Total Residual Chlorine and THMFP7 for Postfilter Chlorination Bench-Scale Study Using Plant Water

As seen above in figures 31 and 32, the majority of the chlorine available was consumed. The increase in chlorine consumption only occurred in the 2.0 mg/L portion of the chlorine spike experiment. The increase in chlorine consumption can be attributed to a high organic loading in the filter house. Since TOC and UV 254 absorbance was not run, conclusions cannot be made. The data collected for the chlorine spike experiments is located in Appendix F.

4.2.3 Summary and Conclusions

The chlorine spike experiment was created to limit a number of the uncontrollable variables associated with normal plant operation in the prefilter chlorination THM study. The normal dose for prefilter chlorination for iron and manganese control at PWSA's treatment plant is 0.3 to 0.5 mg/L for total chlorine introduced before the multimedia filters. On average there was a greater formation of trihalomethanes when the chlorine was added before the filters as opposed to postfilter chlorination. However, the difference in THM potential was normally not beyond the margin for instrument error for the gas chromatography mass spectrometer of 15 to 20% error. This supports the findings in the previous prefilter chlorination THM study that although prefilter chlorination creates more THMs, the increase is not substantial. Provided that the chlorine dose is reasonable, compared to industry standards less than 1.0 mg/L, there are no great THM increases.

To insure optimized treatment for manganese removal, prefilter chlorination should be used and the chlorine dose should be minimized to the point of just removing the iron and manganese. Excessive chlorine should not be used because as seen in the 2.0 mg/L test, the trihalomethane formation potential is excessive.

4.3 DISINFECTION BYPRODUCT PRECURSOR PLANT PROFILE

Organic matter is measured by total organic carbon (TOC) and by UV 254 absorbance. These two tests measure disinfection byproduct precursors because they gage the concentration of organic matter is present in the water and able to be combined with halogens such as chlorine to

create THMs and HAAs. Through different physical and chemical process of the treatment works, organic material is removed. A disinfection byproduct precursor profile was created to show how effective each unit process was at removing organic matter measured by both TOC and UV 254 absorbance.

A tracer study was completed at PWSA to determine how long the water stays in each unit process. The unit process detention times correspond to sampling times to create a disinfection byproduct precursor profile of the PWSA treatment works. The following is a list of the unit processes in the order of water flow and there corresponding detention times.

Table 23: Disinfection Byproduct Precursor Profile and Unit Process Residence Time

Unit Process	Sampling Location	Elapsed Time (hours)	Total Time (hours)
Raw Water	Inlet House	0	0
Coagulation/ Flocculation	Flume	2	2
Sedimentation	Prefilter	39	41
Filtration	Postfilter	2	43
Disinfection	Clear well	8	51

Due to the fluctuating cost of electricity during peak hours. Pumping rates, which uses the greatest amount of the treatment works electricity, vary daily. More water is pumped at night and on weekends to save costs. The variation in pumping rates changes detention times so the above times are accepted averages by the operators and staff at PWSA.

4.3.1 Materials and Methods

The prefilter chlorine is turned off for two days prior to sampling for the disinfection byproduct precursor profile experiment. The two days ensures that the chlorine dosed before the filters does not interfere with the profile by oxidizing organic matter and comprising the TOC and UV 254 absorbance readings.

On the first day at 3:00 PM, the river water was sampled from the inlet house. Day 1 at 3:00 PM is considered time zero for all intents and purposes of this experiment. Two hours later on day 1 at 5:00 PM the flume was sampled. The water in the plant had already been dosed with chemical and rapidly mixed. The flume is where coagulation and flocculation occurs. Next the water flows across Freeport Road to the settling basins where the flocculent particles settle for 39 hours. On day 3 at 8:00 AM water from the top of the filter is sampled. This water has been in the settling basin for 39 hours and has had no contact with chlorine. Two hours later the "pocket of water" has passed through the filter and on day 3 at 10:00 AM water from the bottom of the filter is sampled. After the water has flown through the filter it travels to the chlorine contact chamber where the water flows through a serpentine plug flow reactor for eight hours. On day 3 at 6:00 PM, water is sampled from the end of the clear well right before it goes to distribution.

At each sampling time and location two samples are taken for total organic carbon (TOC) and two samples are taken for UV 254 absorbance. The average of the TOC and UV 254 absorbance measurements were calculated and analyzed. A percent reduction comparing each unit process to the original river level of organic matter was calculated.

4.3.2 Results and Discussion

The following graph represents the total organic carbon plant profile for every unit process in PWSA's water treatment plant. Total organic carbon concentration and ultraviolet 254 nm absorbance are both disinfection byproduct precursors. When they are measured after every unit process in accordance to the elapsed time to ensure the same pocket of water, the result is a profile. The disinfection byproduct precursor profile shows what unit processes are the most important in removing organic matter and minimizing disinfection byproducts such as trihalomethanes from forming.

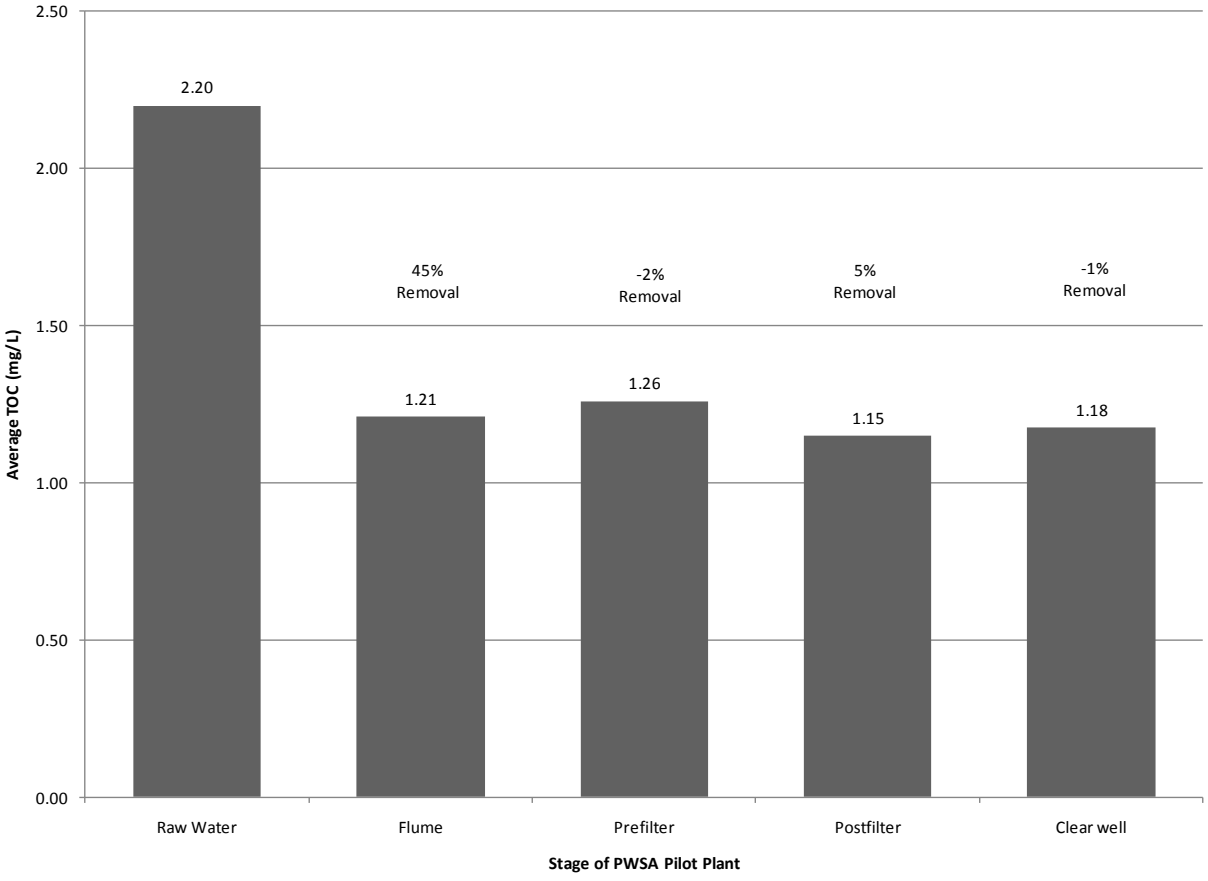

Figure 33. TOC Concentration of PWSA Plant Profile Week of April 27, 2009 Plant-Scale Study

Figure 33 above, shows the TOC plant profile for the week of April 27, 2009. The profile shows that the greatest reduction of TOC occurs in the steps between the raw water intake and the flume. In PWSA's water treatment plant this is the where the chemicals are added and they are rapidly mixed. Chemicals include ferric chloride as a coagulant, lime to adjust the pH, coagulant aide and potassium permanganate to control manganese levels.

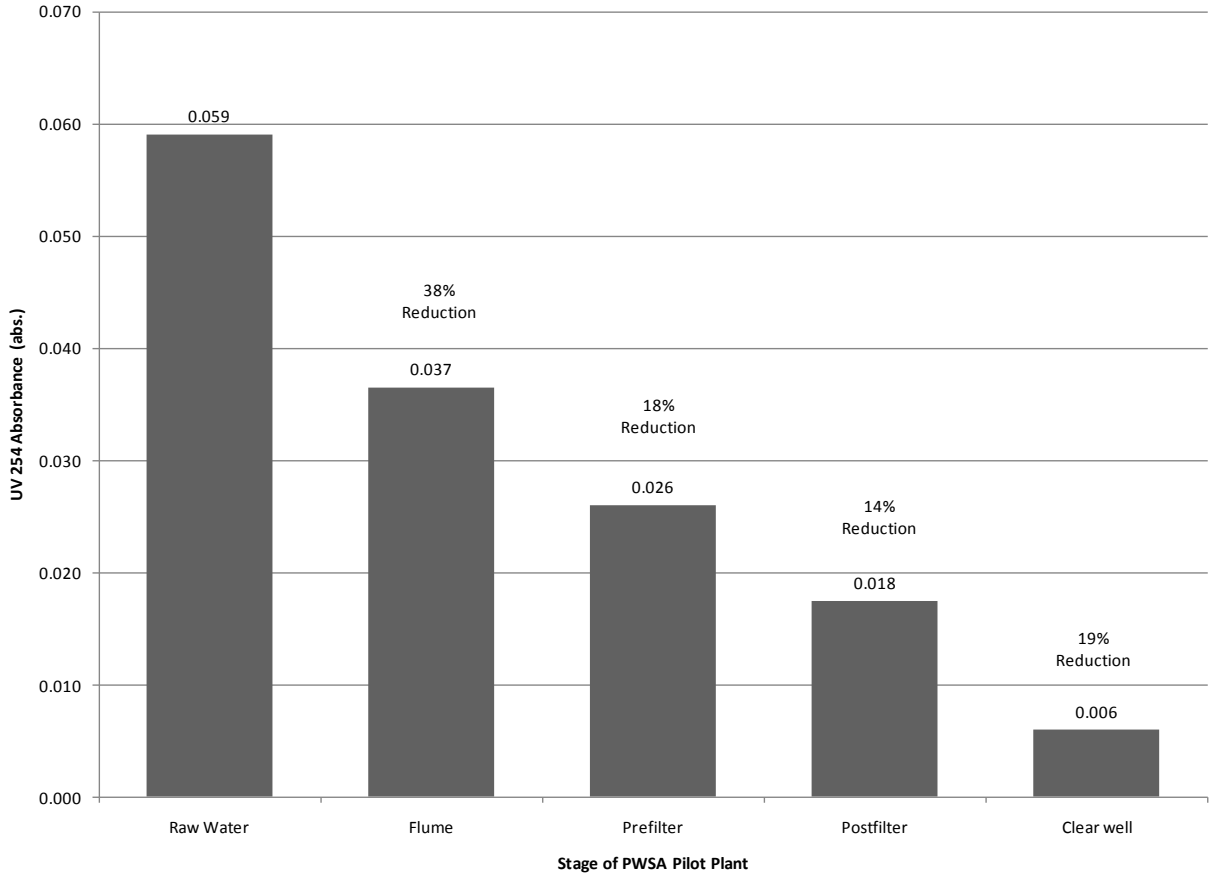

Figure 34. UV 254 Absorbance of PWSA Plant Profile Week of April 27, 2009 Plant-Scale Study

Figure 34 above shows the UV 254 absorbance plant profile for the week of April 27, 2009. The profile shows the percent reduction of total organic carbon between each unit process compared to the original TOC concentration in the raw water, the same as the TOC profile.

Above it is easy to see the greatest reduction, 44%, occurs right after the rapid mix stage. The reduction between postfilter and prefilter water is only 3% which is not significant compared to the original drop after the rapid mix stage. The previously stated fact helps to explain the conclusions in the Prefilter Chlorination THM Study and the Chlorine Spike experiments that there were no significant effects on prefilter chlorination within normal operating chlorine doses.

To make an honest effort to control the THM formation, minimize the chlorine dose like before but work on optimizing the rapid mix process. Ensure all of the paddle mixers are working and the chemicals are dosing correctly.

Figure 35 below shows the TOC plant profile for the week of July 20, 2009. The profile shows that the greatest reduction of TOC occurs in the steps between the raw water intake and the flume. Although the TOC concentrations are not identical to the April 27, 2009 study, the reduction percentages are similar. The greatest reduction in TOC, 44%, occurs right after the rapid mix stage.

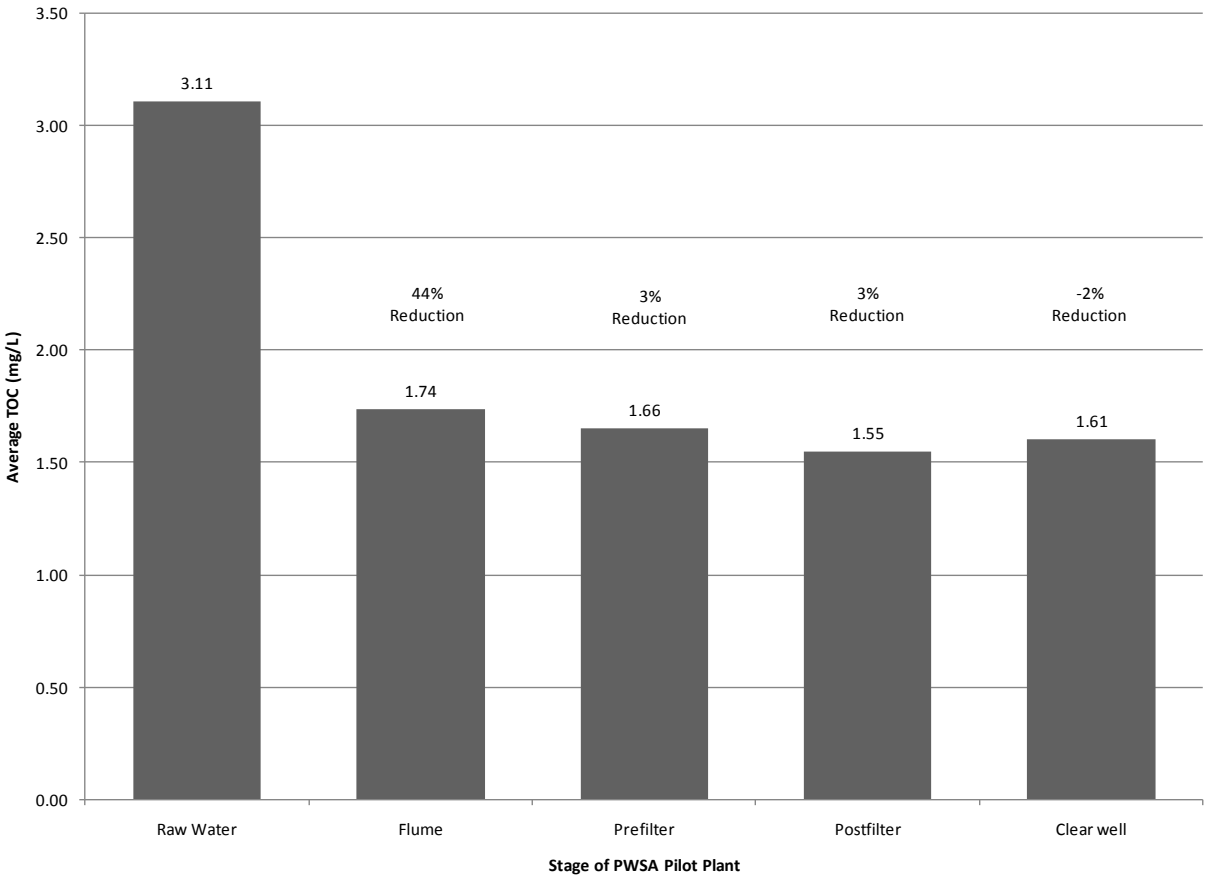

Figure 35. TOC Concentration of PWSA Plant Profile Week of July 20, 2009 Plant-Scale Study

Figure 36 shows the shows the percent reduction of the UV 254 absorbance for the PWSA drinking water plant during the week of July 20, 2009. The greatest reduction of 42% occurs after the rapid mix process, the second greatest reduction in UV 254 absorbance occurs after the sedimentation ponds. Here again, the filters do not remove substantial amounts of organic matter.

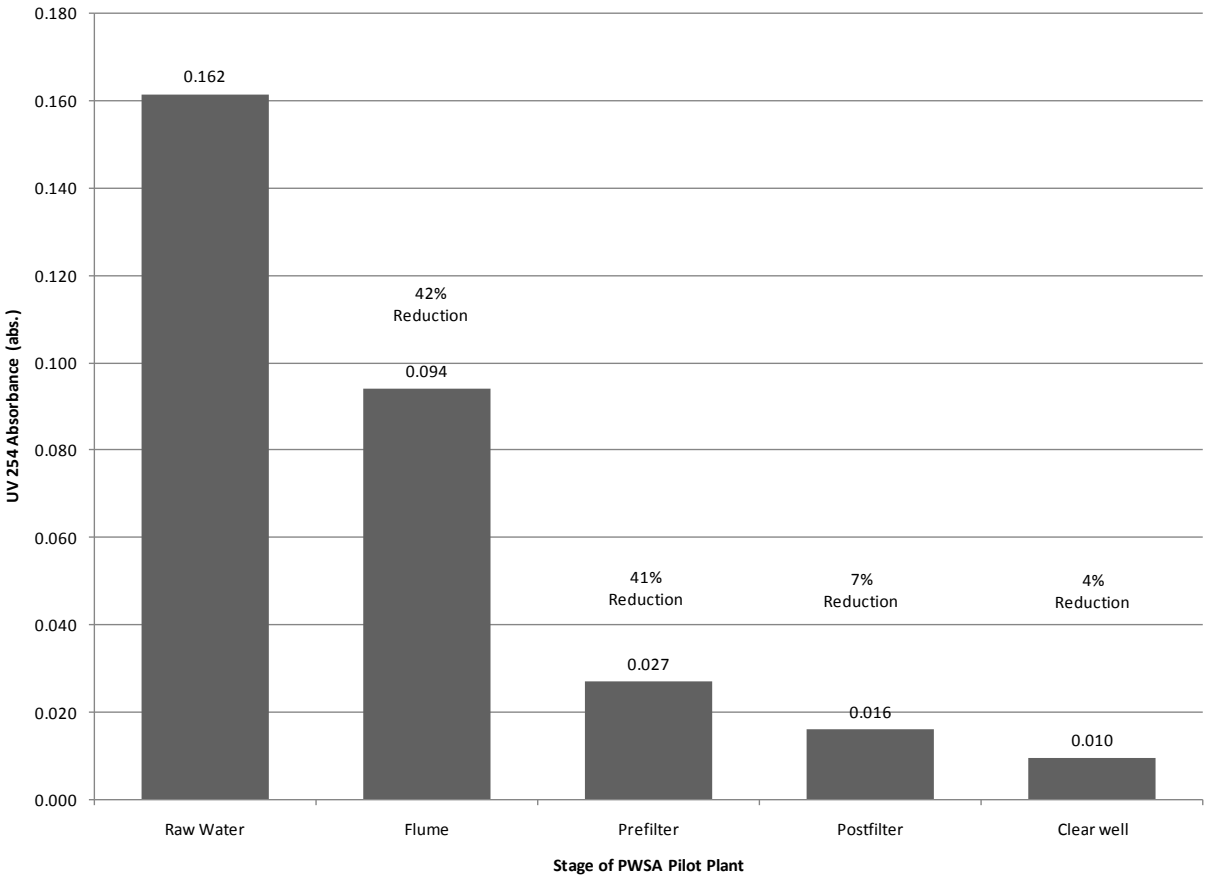

Figure 36. UV 254 Absorbance of PWSA Plant Profile Week of July 20, 2009 Plant-Scale Study

A good way for a plant operator to control THM formation is to be mindful of chlorine dose but more importantly optimize the rapid mix process. Ensure that the all of the mixers are working, the G values have been recalculated and calibrated with respect to rotation speed and paddle surface area. Ensure that the chemical dosing pumps are calibrated and there are no clogs due to chemical build up, especially with lime. Additional graphs and data for the disinfection byproduct precursor experiments are found in Appendix G.

5.0 PILOT-SCALE EXPERIMENTS

5.1 PWSA PILOT PLANT

The pilot plant is located in the PWSA Operations Center. It was designed to simulate the full-scale plant and to allow staff to gain experience and data on how process changes can affect the quality of the treated water. Experimentation using the pilot plant will assist PWSA in developing alternative treatment strategies for the future to meet more stringent drinking water regulations [PWSA, 2000].

Another objective of the pilot plant is to provide a facility that is aesthetically appealing and educational to groups that tour the treatment plant. Therefore the pilot plant is made of transparent materials where possible, and the most aesthetically pleasing unit processes are in clear view of the public [PWSA, 2000].

The pilot plant is setup such that the experimental train will have an ozone system that can be used to study the effect of the oxidant relative to the control process run on the conventional train. The system on the experimental train is set up to allow preozonation or intermediate ozonation. The conventional and experimental trains are separate systems, split at the flow split box from the raw water pumps, until the filters. At the filters the configuration can be changed so that both trains can be run on different filters simultaneously [PWSA, 2000].

The unit processes of the pilot plant are as follows:

- Pumping water from full-scale plant (raw water, primary clarified, secondary clarified, filter effluent for backwash)
- Flow splitting and pretreatment (with chemical feeds)
- Rapid mix (with chemical feeds)
- Flocculation
- Primary clarification (plate settlers)
- Secondary clarification (sedimentation tank)
- Filtration
- Ozonation (pre-ozonation and intermediate ozonation)
- Chlorine dioxide (batch feed) [PWSA, 2000].

Pictures of the PWSA Pilot-Plant are located in Appendix I.

5.1.1 Process Description

Four sources of water are available to the pilot plant from the main plant. They are raw water, primary clarifier effluent, secondary sedimentation effluent (filter influent), and filter effluent (for filter backwashing). The effluent feed to the pilot plant from the main plant's secondary sedimentation and filter processes are gravity based. Raw water and primary clarifier effluent are delivered to the pilot plant by submersible pumps [PWSA, 2000].

The raw water feed is supplied by a 4-inch Myers submersible pump capable of pumping 25 to 80 gpm. The raw water is pumped from a side chamber at the plant's main intake on the Allegheny River. The raw water travels about ¼ mile to the pilot plant location through a 2-inch

PVC line. Turbidity and pH are monitored on the raw influent line and the clarified water line, upstream of the flow splitter box [PWSA, 2000].

The primary clarifier effluent feed is from the plant primary clarifier effluent and is pumped to the pilot plant with a submersible pump. Primary clarifier effluent can be added to the pilot plant between the primary and secondary sedimentation process, or to the filter influent (bypassing secondary sedimentation). The bypassing serves the purpose of using existing plant conditions to test different media configurations or the effect of secondary sedimentation on finished water characteristics. The entire pilot plant would not be required to be in operation to acquire these data [PWSA, 2000].

The secondary clarifier effluent feed is gravity fed as indicated previously from the plant's large secondary sedimentation basins. This can be fed through the pilot filters, thereby allowing pilot data on various filters and finished water quality to be acquired without the use of the entire pilot plant [PWSA, 2000].

The backwash water source for the pilot filter columns is provided from the plant's filtered effluent prior to chlorination. A small centrifugal booster pump has been added to the backwash line immediately upstream of the filter valving to improve backwash pressure and flow rate. The pump is capable of 8.0 gpm at 29.0 feet of head [PWSA, 2000].

5.1.2 Filter Process Description

Filtration is used to remove particles that were not removed during sedimentation. In filtration, water passes through granular filter media, and particulates accumulate either on the surface of the media or are collected through its depth. As particulate matter accumulates in or on the filter media, the pressure drop increases until the available hydraulic head is exhausted or the

particulates begin to break through the media. At that point, the filter media is then cleaned or backwashed and returned to service [PWSA, 2000].

The filter system includes four filters. Two filters are supplied water from the conventional train, while 2 filters are fed water from the experimental train. The flow rate for the filtration process can be varied from 0.2 gpm to 1 gpm, and the filters operate in a constant head, constant rate (effluent flow control) mode. Given that each pilot-scale filter is 6-inches in diameter (I.D.), the process flow range through a filter of 0.2 gpm to 1 gpm represents a corresponding filter loading range 1 gpm/sq. ft to 5 gpm/sq ft. This filter loading range is equivalent to the loading range currently applied on the full-scale filter process [PWSA, 2000].

The influent to the system comes from the upstream processes and enters two filter head control tanks located at either end of the filter column array. The head control tank provides a constant head to the filters. Each head control tank is dedicated to one of the process trains. Two filters for each train can be operated from either head tank by closing and opening specific valves upstream of the filter columns. Both head control tanks have an overflow that allows for any additional flow from the upstream processes that is not needed by the filters to be sent to the plant drain. In the filter influent line, an injection point is present for the addition of a filter aid polymer if it needs to be injected for testing [PWSA, 2000].

Each filter is a 6-inch column made of clear acrylic, approximately 16 feet in total height. Each pilot-scale filter contains 18-inches of anthracite on top of 12-inches of filter sand. This is the same media configuration used in the full-scale filters. However, a ¾ inch thick Leopold Integral Media Support (IMS) cap is used in the pilot scale filter to support these granular layers instead of the 12-inch layer of support gravel used in the full scale filters. The maximum allowable media depth in the filter is 6 feet. The water depth above the filter media can range

from 6.5 to 9.5 feet. A 7.0 foot hydraulic head is maintained above the filter media in both the pilot-scale and full-scale filters [PWSA, 2000].

One of the most important parameters monitored on the filters is the head loss developed during the test run. Head loss is determined by using two pressure transducers and measuring the pressure differential between them. One transducer is located at the highest sample port (above the highest level of media allowed), the other at the lowest sample port, below the IMS Cap under-drain [PWSA, 2000].

The flow is by gravity through the granular media, then through a Leopold IMS Cap under-drain to the effluent line. A filter break tank with a float valve is installed along the effluent line. This break tank provides constant head/flow through the filter. The float and valve configuration in the break tank controls the rate of effluent flow from each filter. As a filter becomes dirty during a filter run, the water level in the break tank decreases causing the float in the break tank to drop. As the float drops, the valve attached to the float opens wider thereby adjusting the rate of effluent flow from the filter [PWSA, 2000].

By adjusting the effluent control valve from the break tank, the operator can control the water level in the tank and thereby control the rate of effluent flow through the particular filter. A rotometer is located downstream of the effluent line to measure the flow. Part of the flow is then drawn off the effluent line to measure turbidity and particle counts. Each filter has a single turbidimeter dedicated to it; particle counters are shared between two filters [PWSA, 2000].

The filtered effluent for each filter is sent to a common collection header that transports filtered water flow to a 350-gallon plastic holding tank or directly to the plant drain. The purpose of the holding tank is to allow the plant to take grab samples or to disinfect the filter

effluent during certain types of studies. The tank overflow goes to the plant drain [PWSA, 2000].

5.1.3 Backwash Protocol

Once the filter has been run for 4 days (approx. 96 hours), it is backwashed according to specification. The filter is drained to 12 inches above the media. Air is backwashed through the bottom of the filter for 3 minutes at 25.5 LPM at 7 psi.

This is followed by the combined air-water wash. This backwash pump is ramped up to 3.6 GPM and the combined air-water wash takes place for 1 minute or until the level reaches the upper flange. This prevents excessive loss of media during backwashes.

The final step is a wash water rinse. Water is pumped from the backwash pump at 3.6 GPM for 5-7 minutes. The water will flow clear by the end of the rinse.

5.2 LIQUID PERMANGANATE PILOT STUDY

The following experiment demonstrates the effectiveness and risks of using potassium permanganate at the top of the filter to oxidize and remove dissolved and particulate manganese.

5.2.1 Materials and Methods

Settled and clarified water flows from the plant into the pilot plant. The settled water flows upwards through a check valve and into the weir, splitter box. From the splitter box the entire flow flows into filter one. The flow is regulated so no water is wasted in overflows set up along the pilot plant. This ensures that 100% of the flow from the weir flows into the filter. Steady state is achieved by not having any water overflow in the weir or the filter and keeping a constant level in the filters.

With this set up all of the flow passes through a calibrated flow meter at the bottom of the filters. The flow reading helps calibrate the dosing pump to ensure an accurate chemical dosage. This pilot plant was calibrated to run similarly to PWSA's treatment plant. At PWSA, the filter loading rate is 1 GPM/ft^2, this is a low loading rate according to industry standards. Because the filter on the pilot plant has an inner diameter of 6 inches, the flow rate through the filter reduced to 0.2 GPM. A filter with a 6 inch inner diameter has a cross sectional area of 0.20 square feet, therefore if the flow is reduced to 0.2 GPM, the filter loading rate is 1 GPM/ft^2.

Pittsburgh Water and Sewer Authority water treatment plant backwashes their filters every 96 hours. Since the filter loading rate is identical on the pilot plant and the full scale plant, the pilot plant filter was backwashed every 96 hours to match the full scale plant. This prevents from excessive turbidity passing through the filter and from filter head loss.

After a backwash is completed, the sampling and experiments begin. On the first day the filter is backwashed twice. Then clarified water runs through the filter until steady state is achieved. Steady state is achieved after 2 hours when the filter and splitter box water levels remain constant. The clarified water has prefilter chlorine already added by the plant. Samples

are taken each day at the top of the filter (weir/splitter box) and the bottom of the filter at the sampling port. The following samples are gathered:

1. Total and Dissolved Manganese
2. Total and Dissolved Iron
3. Free and Total Chlorine
4. Pressure (head loss)
5. TOC
6. UV 254 Absorbance

These measurements will be taken for four days in a row. The next step is to turn off the prefilter chlorine backwash the filter twice, allow the filter to attain steady state and finally gather the following samples:

1. Total and Dissolved Manganese
2. Total and Dissolved Iron
3. Free and Total Chlorine
4. Pressure (head loss)
5. TOC
6. UV 254 Absorbance

Once the prefilter chlorine is off for 24 hours a jar test is completed to determine the recommended dosing of sodium permanganate. This is completed by doing the jar test experiment referenced in section 4.4. Once the recommended dosage of sodium permanganate is determined from the jar test, a day take of dilute sodium permanganate is made. The dilute sodium permanganate solution in the day tank is pumped through a peristaltic metering pump at

a specified rate based on the required dose and the flow rate. The following characteristics were tested:

1. Total and Dissolved Manganese
2. Total and Dissolved Iron
3. Free and Total Chlorine
4. Pressure (head loss)
5. TOC
6. UV 254 Absorbance

5.2.2 Chemical Strength and Dosing Rates

Sodium permanganate is purchased from a chemical supply company in a 20% stock solution. A 20% stock solution is a 200,000 mg/L solution by weight. The stock solution is serially diluted to 2 mg/L into a 20 liter carboy day tank. The dilute 2 mg/L solution of potassium permanganate in the carboy is the new concentration of chemical that will be dosed into the splitter box and weir.

The peristaltic metering pump was calibrated in a 250 mL graduated cylinder to ensure the displayed pumping rate matched the actual pumping rate. The pumping rate was calculated by the concentration of the day tank and the required dose which was determined from previous jar tests.

Manganese removal by permanganate creates a green sand filter effect. A normal multimedia filter containing silica sand and anthracite coal, similar to the ones in PWSA's treatment plant and pilot plant, are treated with permanganate to provide a manganese oxide on the media. Under normal conditions, the coating can be applied by operation for several days

with optimum permanganate feed rates [MWH, 2005]. Partial or marginal treatment may occur during the coating process. Once the coating is applied completely, satisfactory removals are usually maintained. The process is more efficient at pH values above 7.5 [MWH, 2005].

The applied of permanganate should be controlled carefully because permanganate gives an easily detectable pink color in water at concentrations in the 0.05 mg/L range. Controlling the dose range is critical in avoiding consumer complaints [MWH, 2005].

5.2.3 Results and Discussion

Pittsburgh Water and Sewer Authority just like many other drinking water plant utilities across the country uses prefilter chlorination to oxidize iron and manganese. The oxidized metals, in solid form now, are removed on multimedia filters.

In order to complete the many jar, pilot and full scale experiments the prefilter chlorine needed to be turned off on PWSA's water treatment plant. The turning off of prefilter chlorination was to ensure chlorine was not present unless it as purposefully added. A limitation to the experiments in PWSA was that the prefilter chlorine could only be off at maximum four days because manganese would start to pass through the filters and out into the distribution system. If the prefilter chlorine was not turned back on, customers and residents of Pittsburgh would call and complain of "tea colored" water.

The point being of the previous paragraph is that if there is not an oxidizing agent present at the top of the filters such as chlorine, dissolved iron and manganese will pass through the filters and violate EPA secondary pollutant standards.

In previous studies, namely the hydrogen peroxide at varying pH jar tests, hydrogen peroxide was tested as a manganese oxidizer. The jar test proved to be a failure, manganese is not oxidized by hydrogen peroxide within normal operating pH levels.

The jar tests concerning sodium permanganate at different doses proved that if the proper dose could be determined and dosed accurately, 100% manganese oxidation and removal is possible. Liquid permanganate dosed at the tops of the filters would provide manganese oxidation without increasing the THM potential.

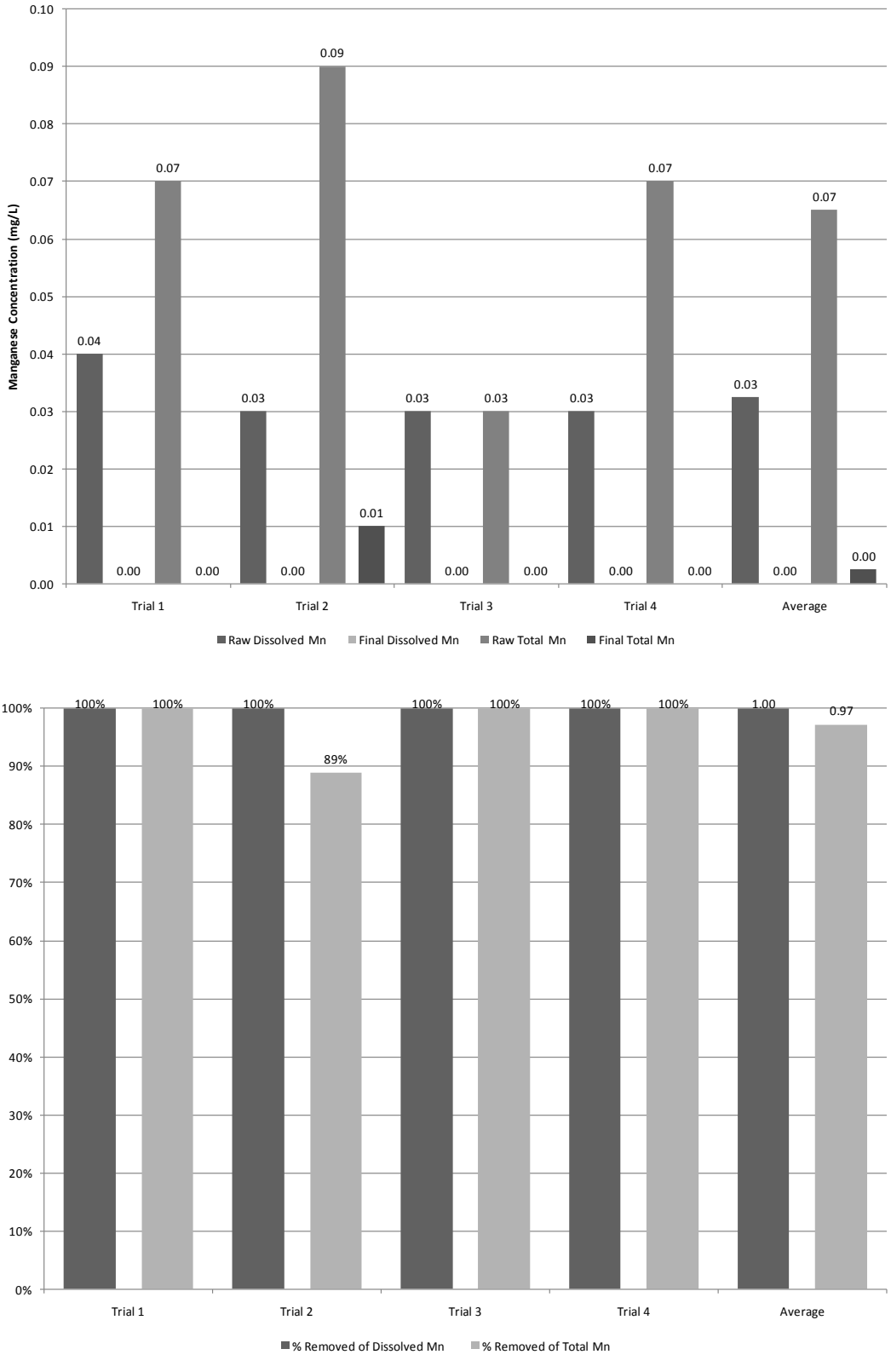

Figure 37. Removal of Total and Dissolved Manganese Using Prefilter Chlorine Oxidant Pilot-Scale Study

Figure 37 above shows the manganese removal in the pilot plant when the prefilter chlorine was on and optimized. For most cases, there was 100% removal of dissolved manganese and 97% removal of total manganese. The above graphs prove that prefilter chlorination is an effective means of removing excessive manganese in drinking water plants. Other experiments previously discussed conclude that prefilter chlorination is not a significant cause of THM formation.

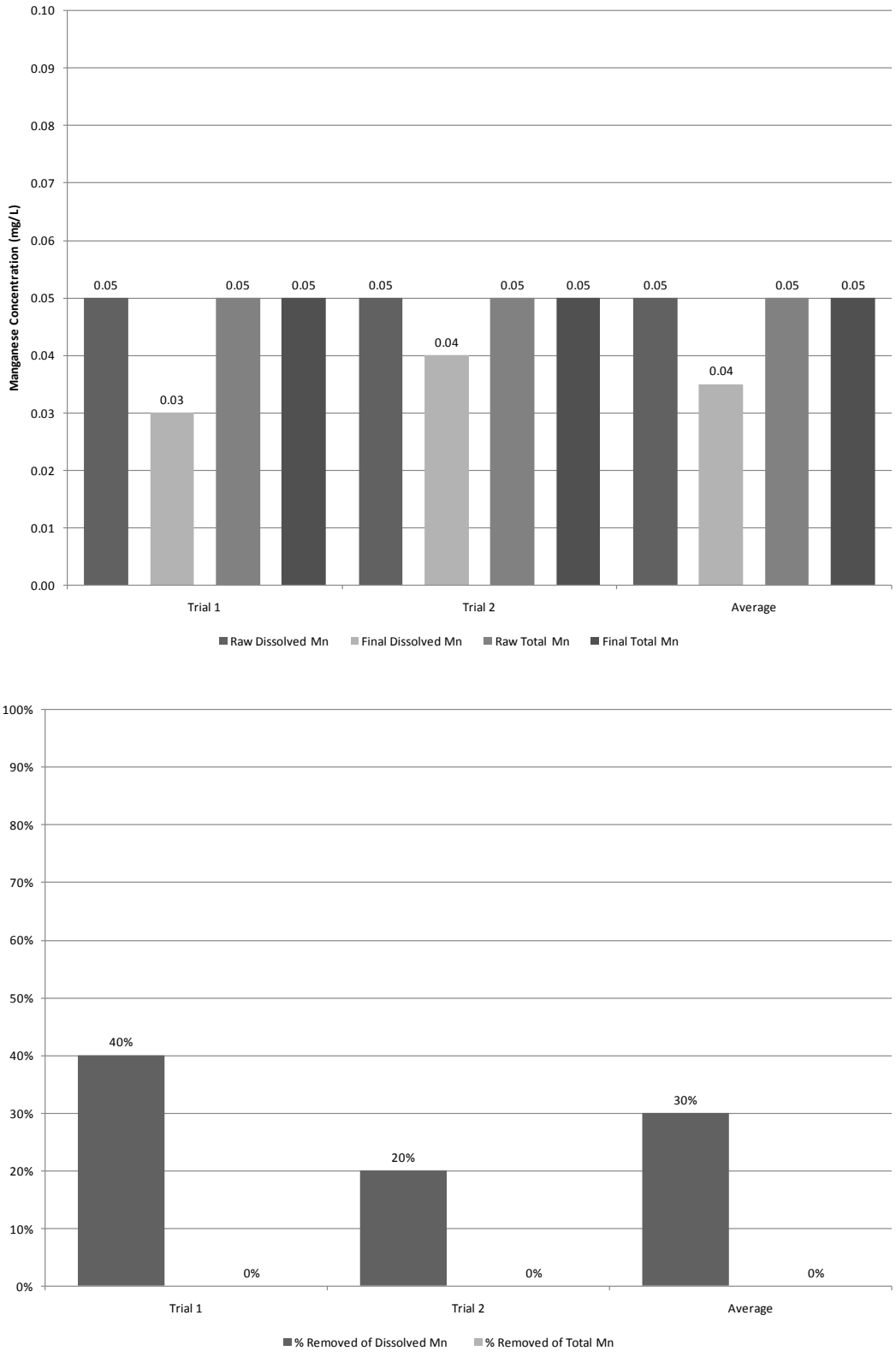

Figure 38. Removal of Total and Dissolved Manganese Using No Oxidant Pilot-Scale Study

As stated in the anecdote above, when prefilter chlorination is off, there is very little manganese removal and manganese passes through the filters and out to the distribution system. Figure 38 shows that on average there was only 30% removal of dissolved manganese and no removal of total manganese. With no oxidizing agent, there is no manganese removal in the filters. Having no oxidizing agent present for prefilter water is not a viable option for water treatment utilities.

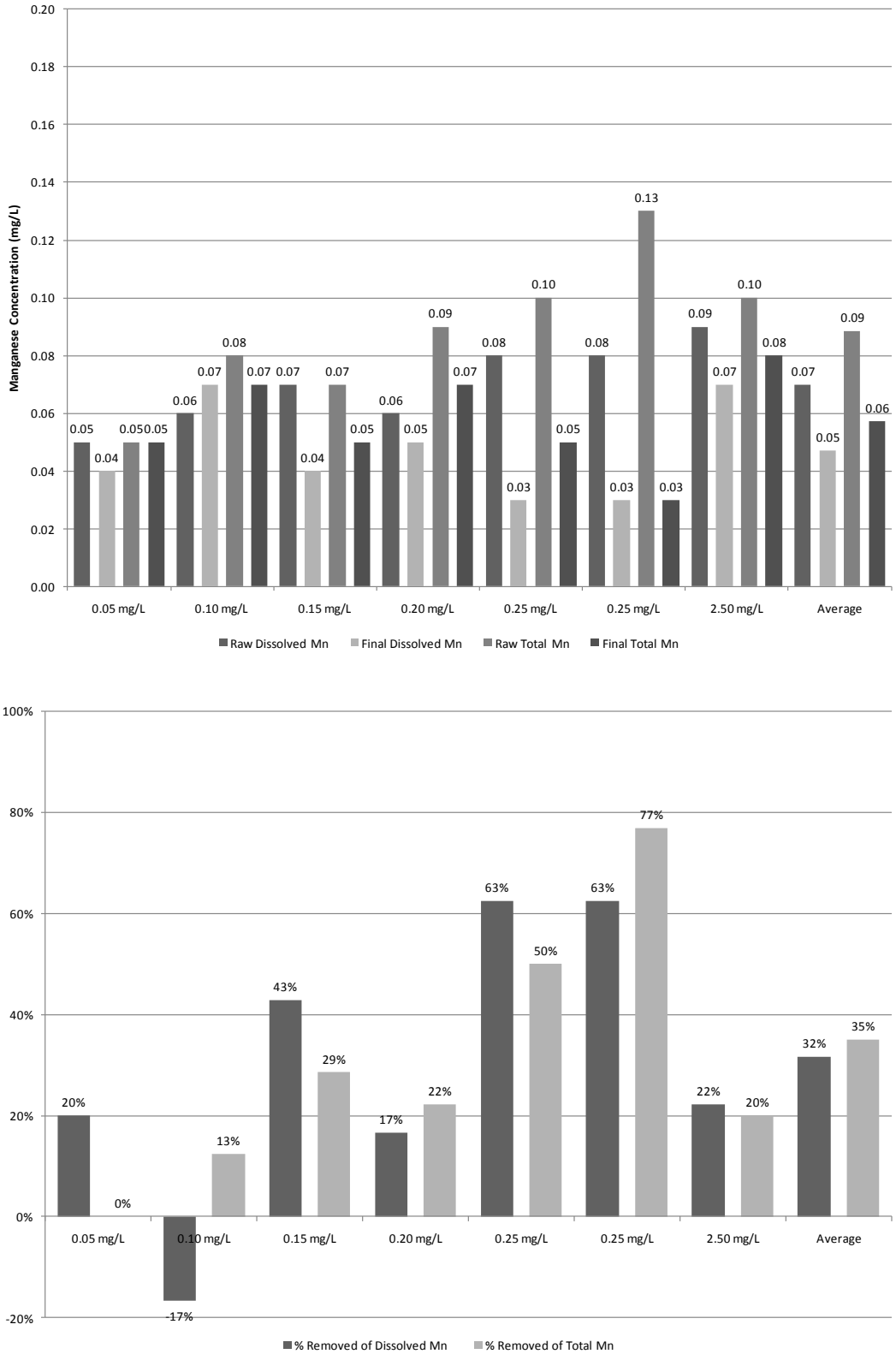

Figure 39. Removal of Total and Dissolved Manganese Using Liquid Sodium Permanganate Oxidant at Varying Dose Pilot-Scale Study

The crux of this experiment was to determine the correct dose of sodium permanganate needed to oxidize and remove manganese on the pilot plant multimedia filters. Bench-scale studies were conducted to determine the correct dosage of permanganate to oxidize the manganese in the prefilter water. After incomplete removal of manganese at 0.25 mg/L doses, lighter doses were tested also to no avail.

The first time the experiment was run, a calculation error occurred and 2.50 mg/L of sodium permanganate was dosed instead of 0.25 mg/L. This shows that if an operator accident occurs and the liquid permanganate is overdosed, there will be insufficient manganese removal and even possibly an increase in manganese. A miscalculation in the strength of the day tank resulted in an overdose of chemical by ten times the recommended amount. The water above the filter was light pink and the post filter water was tea colored. This is a risk of "removing manganese with manganese."

Provided that the optimum dosage of liquid permanganate could be determined and well regulated at a water treatment plant, there is a possibility for adequate manganese removal, but the risk of operator error is too great for a utility to chance this method. Dosing pumps would have to be regularly calibrated and serial dilutions for accurate concentration dosing would have to be regularly checked. Manganese levels both reduced and total would need to be monitored multiple times throughout the day to ensure proper treatment.

In Figure 39 seen above, there is no dose of sodium permanganate found to completely oxidize manganese. In the permanganate bench-scale study in section 3.4, there was definitely a dose of permanganate used to attain 100% oxidation. The problem with the pilot-scale study is that there are too many variables. The pump, although calibrated every day, is a variable. The day tank of sodium permanganate has run dry on occasion and the dosing is compromised. The

previous examples that occurred in a pilot-scale study serve as a foreshadowing to the complications an operator would experience on a plant-scale project.

As discussed in previous experiments, the trihalomethane concentration increase is not excessive due to prefilter chlorination. The disinfection byproduct precursor profile showed that most of the organic matter is removed in the flume. It is imperative in order to minimize disinfection byproducts to optimize chemical feed systems and rapid mix systems.

5.2.4 Pilot-Scale Studies Insight to Operators

The correct dose of liquid sodium permanganate is difficult to maintain. In order to maintain the constant dose, continuous calibration of the chemical dosing pumps and Atomic Adsorption tests on the prefiltered and post-filtered water need to be implemented in order to scale up the pilot-scale study to a full plant operation. Additional operators would be needed on PWSA's staff to carry out duties mentioned above.

Prefilter chlorination allows for the oxidation of manganese without the fear of overdosing chemical and passing permanganate. Provided that the dose of sodium hypochlorite is dosed minimally, no significant byproducts are created.

6.0 SUMMARY AND CONCLUSIONS

The overall objective of this research is to explore manganese removal alternatives applicable to PWSA and to optimize manganese removal in accordance with DBP limits. In accordance with EPA's Stage 2 Disinfectants and Disinfection Byproducts Rule, the levels of THMs and HAAs need to be minimized. Although free chlorine provides adequate oxidation of manganese, the DBP formation is harmful to human health and is in violation of the EPA. Alternatives for manganese removal needed to be explored. The purpose of researching manganese and water treatment optimization with respect to disinfection byproducts was to provide a real world useable solution to utilities across the nation.

- Prefilter chlorination, a practice that is used across the country to remove elevated concentrations of manganese in drinking water uses a low dose (lower than disinfection) of chlorine before the filters to oxidize both iron and manganese. The oxidized metals are removed on the multimedia filters. From both the THM prefilter chlorination plant study and the chlorine spike experiment, the increase in THM formation potential of water that has been prefilter chlorinated is not substantial to waters that have not been prefilter chlorinated. If the dose is kept reasonable (below 0.5 mg/L), there is no apparent increase of THMs outside of the instrument error margin.
- PWSA wanted to find a find a coagulant that does not contain excessive manganese contamination the way ferric chloride does. Ferric sulfate and ferric chloride were tested

in a bench-scale study. Ferric sulfate proved to contain less manganese concentration than ferric chloride. Full plant records kept by PWSA often show an increase of manganese in the flume, greater than the manganese concentration in the raw water. The manganese concentration increase can be partly attributed to the manganese contamination in the coagulant ferric chloride. Another cause for the increase in manganese concentration in the flume could be due to using potassium permanganate at lower pH levels for enhanced coagulation. Ferric chloride is known throughout the water treatment industry to be a manganese contaminated coagulant [States, 2009]. Ferric sulfate, although slightly more expensive contains far less manganese contamination. If a utility is trying all means necessary to reduce manganese passing without excessive chlorination, changing coagulants to a cleaner option such as ferric sulfate is a viable solution to aid in treatment optimization.

- PWSA also wanted to test a novel technology to oxidize and remove manganese from drinking water. Hydrogen peroxide was tested in jars at varying doses and varying pH levels. Hydrogen peroxide is a stronger oxidant than free chlorine and does not create any regulated byproducts. The previous facts alone should have meant that the solution to prefilter chlorination lies with hydrogen peroxide oxidation of manganese. Through many bench-scale tests, hydrogen peroxide only oxidized iron and never oxidized manganese. The point needs to be brought up that hydrogen peroxide oxidizes free chlorine. Hydrogen peroxide has a larger oxidation potential than chlorine and when it reacts with chlorine it yields the chloride ion which is useless in disinfection. If the hydrogen peroxide did in fact oxidize manganese it would still not be practical to use in a water treatment plant that uses disinfection by free chlorine. The half-life of hydrogen

peroxide ranges from 8 hours to 20 days depending on the microbiological activity and metal contamination of the water [FMC Corporation, 2008]. Even a 24 half-life is far too long for a chemical that comprises disinfection.

- Another objective was to investigate an old successful technology and adapt it for PWSA's needs. Sodium permanganate, a fully dissolved permanganate solution, was dosed at the top of the filter to oxidize and remove the reduced manganese in the settled water. This experiment was completed on jar tests and at pilot-scale. Additional tests were devised to prevent overdosing by using a lower dose of prefilter permanganate and increasing the pH level. The liquid sodium permanganate bench-scale tests worked exceptionally well. The results showed, as predicted, the manganese breakthrough phenomenon that occurs when permanganate was used to remove manganese. The pilot-scale experiments were difficult to control and insufficient manganese removal occurred. With better monitoring and better chemical feed calibration sodium permanganate introduced prefilter should be able to remove manganese in drinking water. A major concern with using permanganate to remove manganese in drinking water is the fear of overdosing permanganate. When the pH is elevated, a lessened dose of permanganate was required to oxidize manganese. A small increase in pH, from 6.8 to 7.2 results in total oxidation of manganese. Elevating the prefilter pH with caustic soda and dosing 0.05 to 0.10 mg/L of permanganate prefilter could provide a safe alternative for manganese oxidation and removal.
- The fifth and final specific objective was to determine the most effective steps to minimize THM formation. Experiments that analyzed prefilter chlorination and optimized unit process for removal of organic carbon measure by TOC and UV 254

absorbance. Previous research created a tracer study for the water treatment plant at PWSA. The tracer study dictated a certain amount of time that a pocket of water would spend in each unit process. This timeline dictated the TOC and UV 254 disinfection byproduct precursor plant profile experiment. Though both indicators on separate occasions, the data concludes that the greatest removal of disinfection byproduct precursor occurs after the rapid mix in the coagulation flocculation steps. In order to minimize THM formation potential, the rapid mix coagulation flocculation steps need to be optimized. Chemicals include ferric chloride as a coagulant, lime to adjust the pH, coagulant aide and potassium permanganate to control manganese levels. To make an honest effort to control the THM formation, minimize the chlorine dose like before but work on optimizing the rapid mix process. Ensure all of the paddle mixers are working and the chemicals are dosing correctly. Ensure that the all of the mixers are working, the G-values have been recalculated and calibrated with respect to rotation speed and paddle surface area. Ensure that the chemical dosing pumps are calibrated and there are no clogs due to chemical build up, especially with lime.

7.0 RECOMMENDATIONS FOR FUTURE WORK

The above research was conclusive; however it did open new doors for new scientific exploration. Below is a short list of recommendations for future work.

- PWSA alters its pumping and flow rates throughout the week and throughout the day to cut costs on electricity during peak hours. The variation in pumping affects the flow rates through each unit process therefore changing the residence time of each unit process. A complete a full tracer study throughout the week to see the amount of time a pocket of water spends in each unit process when the pumping rate is changing. In addition to the tracer study, a complete plant analysis should be completed to see how treatment is compromised when the plant is not running at steady state conditions.
- Although the conclusions from the ferric chloride and ferric sulfate bench-scale studies make a good case for using ferric sulfate, additional pilot-scale studies should be carried out to ensure that ferric sulfate is a suitable alternative for ferric chloride. In particular, ferric sulfate should be tested in enhanced coagulation settings.
- Finally, the bench-scale studies with the low dose of either prefilter chlorine or prefilter permanganate should be scaled-up to a pilot scale. Pilot scale results are a closer representation to the results on a full-scale plant. The pilot-scale study will allow

operators to see the drawbacks of oxidizing manganese in this fashion before it implemented plant-scale.

8.0 ENGINEERING IMPLICATIONS

PWSA and the University of Pittsburgh explored ways to remove manganese while remaining contentious of forming trihalomethanes. Prefilter chlorination for reasons of effectiveness, cost, and ease of operation remains a very popular means of removing manganese from drinking water. Provided that the dose of chlorine added for manganese oxidation is minimized and the rapid mix stage of plant is optimized for TOC removal, trihalomethanes will not be problem of manganese removal.

Hydrogen peroxide is not a suitable oxidant for manganese removal in drinking water. Hydrogen peroxide oxidizes iron but not manganese, also hydrogen peroxide reacts with chlorine used for disinfection. The half-life of hydrogen peroxide is too long to use it before chlorine disinfection. Even if it did oxidize manganese it still would not be practical in a plant-scale application.

Ferric sulfate does contain less manganese contamination than ferric chloride. It is a viable alternative coagulant to ferric chloride to help minimize the amount of manganese that needs to be removed.

Liquid sodium permanganate can be dosed before the filters to oxidize manganese. However, the dose needs to be exactly correct and many checks need to be made to ensure an operator is not under of overdosing the chemical. Practically, prefilter sodium permanganate is not a good choice for manganese removal. Too much can go wrong on the operators side and

there are not extra steps taken to remove manganese if it passes through the filters. Prefilter chlorine is a better alternative for manganese removal.

The greatest amount of organic matter, both TOC and UV 254 absorbance, is removed during the rapid mix and coagulation/flocculation stage. Since TOC and UV 254 absorbance is a precursor for trihalomethanes, it is of great importance to optimize treatment in the rapid mix and coagulation/flocculation stage. Ensure the pumps are dosing correctly, ensure that the paddles are running at the correct speeds and ensure there is adequate residence time in each unit process.

EXPERIMENTAL DATA APPENDIX

Throughout the research, a lot of information was gathered and calculated that could not be included in the main sections of this thesis. In the following Appendices are additional charts and experiments that did not fit the focus of the research.

APPENDIX A

A.1 IMHOFF CONE AND PLANT SETTLED WATER JAR TESTS

It was important to see how closely the jar tests and settling cones mimicked the water plant. Some results in the first experiment such as higher turbidity and iron and concentrations in the jars that used the Imhoff cones were observed. Note: although the turbidity was not measured in this set of jar tests, jars 1-4 were visibly more turbid than 5 and 6. At first the thought was that chlorine was oxidizing the iron and manganese and creating better quality water. To make sure, this hypothesis was tested with a simple jar test. The objective was to see if having the flume water settle in an Imhoff cone for the same detention time as the settling basin will produce water of the same quality.

A.1.1 Materials and Methods

Four jars were used in this test. Jars 1 and 2 were made from water in the flume that was sampled from ¾ depth of the flume and transferred to an Imhoff cone. Jars 3 and 4 were collected 24 hours later on top of the filter after it had spent 24 hours in the settling basin. Jars 1-4 are all from the same pocket of water. The prefilter chlorine was turned off for 3 days and there was no chlorine residual present in the flume or on top of the filter at the time of the tests. Basic wet chemistry analyses were performed on all jars. The following lists the parameters:

a. Temperature

b. pH

c. Alkalinity

d. Turbidity

e. Dissolved Iron

f. Total Iron

g. Dissolved Manganese

h. Total Manganese

i. Total Organic Carbon

j. Free Chlorine

k. Total Chlorine

A.1.2 Results and Discussion

The following data was gathered from the jar tests that compare laboratory conditions to plant conditions with regard to plant and Imhoff settling.

Table 24. Imhoff Cone Jar Test Data

		Imhoff Settled 1	Imhoff Settled 2	Basin Settled 1	Basin Settled 2
Temp	**(°C)**	17	17	15	16
pH	**(pH)**	6.90	7.03	6.69	6.69
Alkalinity	**(Ca as CaCO3)**	39	38	37	38
Turbidity	**(NTU)**	2.900	2.450	0.534	0.585
Fe Diss	**(mg/L)**	0.02	0.00	0.01	0.00
Fe Total	**(mg/L)**	0.91	0.92	0.16	0.21
Mn Diss	**(mg/L)**	0.04	0.04	0.02	0.03
Mn Total	**(mg/L)**	0.07	0.06	0.04	0.03
TOC	**(mg/L)**	2.42	2.31	1.24	1.90
Chlorine	**(mg/L)**	DND	DND	DND	DND
Chlorine	**(mg/L)**	DND	DND	DND	DND

The temperature of the Imhoff cones was slightly greater than the settled water because the plant water was settling outside in November and the Imhoff cone was settling on a lab bench. Since there was no prefilter chlorine on in the plant there was no chlorine residual. This was important because the theory in the previous jar tests was that chlorine was affecting the analyses.

The alkalinity for all the jars was the same which was expected since no lime or soda ash is added between the flume and the top of the filter. The turbidity is a different story. The water from the Imhoff cones was visibly orange in color. The turbidity readings from the Imhoff cones were five to six times greater than the settled water sampled from the top of the filters. The orange color is most likely iron from the raw water and from the ferric chloride added as a coagulant.

The dissolved iron for all jars was approximately equal only varying by 0.02 mg/L. However, the total iron in the Imhoff cones was 4 to 5 times greater than the plant settled water. The total manganese in the Imhoff cones is about twice the amount in the settled water. Even the total organic carbon is greater in the Imhoff settled jars.

A.1.3 Summary and Conclusions

The Imhoff cone does not give a good representation of the settling that occurs at PWSA's water treatment plant. An additional test was made that kept the water in an Imhoff cone for 72 hours. The turbidity was still 3 times larger than plant settled water.

These findings voided the first jar test performed, hydrogen peroxide and prefilter chlorine on the issue that the water was not the same in terms of turbidity, iron content, manganese content and TOC. This test shows that the only way to test settled water before the filter is to turn off the prefilter chlorine and sample from the top of the filter.

APPENDIX B

B.1 HYDROGEN PEROXIDE BENCH-SCALE DATA

B.1.1 Hydrogen Peroxide at 3.0 mg/L Dose Bench-Scale Data

Table 25. Hydrogen Peroxide 3.0 mg/L Dose at Varying pH Bench-Scale Test: 12 January 2009

Configuration		Jar 1 pH 6.8	Jar 2 pH 6.8 + H2O2	Jar 3 pH 7.2	Jar 4 pH 7.2 + H2O2	Jar 5 pH 7.6	Jar 6 pH 7.6 + H2O2
Actual pH	**(pH)**	6.85	6.80	7.21	7.17	7.60	7.60
Temp	**(°C)**	6.6	7.1	7.7	8.7	9.0	10.2
Mn Diss	**(mg/L)**	0.04	0.06	0.04	0.05	0.05	0.06
Mn Total	**(mg/L)**	0.06	0.06	0.05	0.05	0.06	0.06
Fe Diss	**(mg/L)**	0.00	0.02	0.02	0.02	0.04	0.00
Fe Total	**(mg/L)**	0.29	0.32	0.21	0.22	0.30	0.29
TOC	**(mg/L)**	1.85	2.60	19.70	6.08	2.44	2.32
UV 254	**(abs.)**	0.018	0.020	0.018	0.012	0.011	0.008

Table 26. Hydrogen Peroxide 3.0 mg/L Dose at Varying pH Bench-Scale Test: 13 January 2009

Configuration		Jar 1 pH 8.0	Jar 2 pH 8.0 + H2O2	Jar 3 pH 8.4	Jar 4 pH 8.4 + H2O2	Jar 5 pH 8.8	Jar 6 pH 8.8 + H2O2
Actual pH	**(pH)**	7.98	8.02	8.41	8.40	8.86	8.90
Temp	**(°C)**	5.0	8.1	8.9	9.5	10.2	11.0
Mn Diss	**(mg/L)**	0.03	0.03	0.01	0.03	0.03	0.03
Mn Total	**(mg/L)**	0.04	0.04	0.03	0.03	0.03	0.03
Fe Diss	**(mg/L)**	0.00	0.00	0.02	0.01	0.00	0.00
Fe Total	**(mg/L)**	0.12	0.12	0.13	0.20	0.14	0.16
TOC	**(mg/L)**	1.50	1.48	1.47	1.51	1.48	1.49
UV 254	**(abs.)**	0.002	0.002	0.003	0.006	0.004	0.011

B.1.2 Hydrogen Peroxide at 6.0 mg/L Dose Bench-Scale Data

Table 27. Hydrogen Peroxide 6.0 mg/L Dose at Varying pH Bench-Scale Test: 2 March 2009

Configuration		Jar 1 pH 6.8	Jar 2 pH 6.8 + H2O2	Jar 3 pH 7.2	Jar 4 pH 7.2 + H2O2	Jar 5 pH 7.6	Jar 6 pH7.6 + H2O2
Actual pH	**(pH)**	6.81	6.89	7.15	7.21	7.61	7.60
Temp	**(°C)**	8.6	7.9	8.0	8.2	8.5	9.1
Raw TOC	**(mg/L**	1.25	1.25	1.24	1.20	1.25	1.26
Raw UV 254	**(abs.)**	0.18	0.21	0.17	0.19	0.18	0.18
Raw Turbidity	**(NTU)**	0.58	0.50	0.57	0.52	0.54	0.53
Mn Diss	**(mg/L)**	0.04	0.04	0.02	0.05	0.03	0.06
Mn Total	**(mg/L)**	0.06	0.06	0.04	0.05	0.03	0.06
Fe Diss	**(mg/L)**	0.04	0.00	0.00	0.03	0.00	0.00
Fe Total	**(mg/L)**	0.13	0.19	0.15	0.15	0.10	0.19
Final Turbidity	**(NTU)**	0.25	0.24	0.12	0.11	0.11	0.09
Final H2O2	**(mg/L)**	0.0	6.0	0.0	5.5	0.0	5.5
Final pH	**(pH)**	7.12	6.98	7.11	7.20	7.21	7.41
Final TOC	**(mg/L)**	2.05	1.44	1.49	1.52	1.50	1.53
Final UV 254	**(abs.)**	0.016	0.017	0.013	0.018	0.015	0.018

Table 28. Hydrogen Peroxide 6.0 mg/L Dose at Varying pH Bench-Scale Test: 3 March 2009

Configuration		Jar 1 pH 8.0	Jar 2 pH 8.0 + H2O2	Jar 3 pH 8.4	Jar 4 pH 8.4 + H2O2	Jar 5 pH 8.8	Jar 6 pH 8.8 + H2O2
Actual pH	**(pH)**	7.95	8.03	8.37	8.44	8.83	8.79
Temp	**(°C)**	4.2	4.8	6.1	6.4	6.4	5.9
Raw TOC	**(mg/L**	1.17	1.20	1.25	1.21	1.24	1.20
Raw UV 254	**(abs.)**	0.31	0.32	0.32	0.31	0.33	0.34
Raw Turbidity	**(NTU)**	0.54	0.54	0.52	0.42	0.48	0.51
Mn Diss	**(mg/L)**	0.04	0.05	0.04	0.05	0.03	0.04
Mn Total	**(mg/L)**	0.05	0.06	0.05	0.06	0.04	0.04
Fe Diss	**(mg/L)**	0.00	0.00	0.00	0.00	0.03	0.02
Fe Total	**(mg/L)**	0.14	0.16	0.17	0.14	0.20	0.19
Final Turbidity	**(NTU)**	0.45	0.51	0.33	0.28	0.29	0.41
Final H2O2	**(mg/L)**	0.0	5.0	0.0	6.0	0.0	4.5
Final pH	**(pH)**	7.43	7.63	7.74	7.53	8.16	8.04
Final TOC	**(mg/L)**	1.60	1.59	1.51	1.55	1.73	1.58
Final UV 254	**(abs.)**	0.017	0.023	0.018	0.020	0.018	0.020

APPENDIX C

C.1 FERRIC CHLORIDE AND FERRIC SULFATE JAR TEST DATA

Table 29. Ferric Sulfate and Ferric Chloride Jar Test: 12 February 2009

Type		Jar 1 Ferric Chloride +	Jar 2 Ferric Chloride +	Jar 3 Ferric Chloride	Jar 4 Ferric Sulfate +	Jar 5 Ferric Sulfate +	Jar 6 Ferric Sulfate
Raw pH	**(pH)**	7.76	7.76	7.76	7.76	7.76	7.76
Raw Mn Diss	**(mg/L)**	0.15	0.15	0.16	0.14	0.15	0.15
Raw Mn Total	**(mg/L)**	0.16	0.15	0.16	0.15	0.16	0.15
Raw Fe Diss	**(mg/L)**	0.02	0.01	0.03	0.01	0.02	0.02
Raw Fe Total	**(mg/L)**	0.67	0.69	0.68	0.70	0.67	0.66
Raw Turbidity	**(NTU)**	26.30	26.30	26.30	26.30	26.30	26.30
Raw TOC	**(mg/L)**	2.43	2.43	2.43	2.43	2.43	2.43
Raw UV 254	**(abs.)**	0.17	0.17	0.17	0.14	0.15	0.14
Adjusted pH	**(pH)**	6.67	6.66	6.65	6.66	6.66	6.65
Potassium Permanganate	**(mg/L)**	0.70	0.70	0.00	0.70	0.70	0.00
Ferric Chloride	**(mg/L)**	25.00	25.00	25.00	0.00	0.00	0.00
Ferric Sulfate	**(mg/L)**	0.00	0.00	0.00	25.00	25.00	25.00
Final pH	**(pH)**	6.64	6.63	6.80	6.78	6.63	6.69
Final Mn Diss	**(mg/L)**	0.00	0.01	0.21	0.00	0.00	0.18
Final Mn Total	**(mg/L)**	0.20	0.27	0.21	0.25	0.26	0.18
Final Fe Diss	**(mg/L)**	0.03	0.05	0.01	0.00	0.00	0.03
Final Fe Total	**(mg/L)**	0.26	0.24	0.20	0.10	0.10	0.06
Final Turbidty	**(NTU)**	1.42	2.13	1.02	1.51	2.00	1.03
Final TOC	**(mg/L)**	1.41	1.45	1.41	1.42	1.45	1.37
Final UV 254	**(abs.)**	0.042	0.045	0.025	0.039	0.045	0.031

Table 30. Ferric Sulfate and Ferric Chloride Jar Test: 16 February 2009

Type		Jar 1 Ferric Chloride +	Jar 2 Ferric Chloride +	Jar 3 Ferric Chloride	Jar 4 Ferric Sulfate +	Jar 5 Ferric Sulfate +	Jar 6 Ferric Sulfate
Raw pH	**(pH)**	7.02	7.02	7.02	7.02	7.02	7.02
Raw Mn Diss	**(mg/L)**	0.10	0.14	0.13	0.10	0.10	0.10
Raw Mn Total	**(mg/L)**	0.11	0.15	0.13	0.12	0.12	0.11
Raw Fe Diss	**(mg/L)**	0.04	0.03	0.05	0.04	0.04	0.04
Raw Fe Total	**(mg/L)**	0.81	0.79	0.81	0.80	0.81	0.82
Raw Turbidity	**(NTU)**	38.40	38.40	38.40	38.40	38.40	38.40
Raw TOC	**(mg/L)**	3.41	3.41	3.41	3.41	3.41	3.41
Raw UV 254	**(abs.)**	0.12	0.12	0.12	0.12	0.12	0.12
Adjusted pH	**(pH)**	6.65	6.67	6.69	6.69	6.65	6.65
Potassium Permanganate	**(mg/L)**	0.70	0.70	0.00	0.70	0.70	0.00
Ferric Chloride	**(mg/L)**	25.00	25.00	25.00	0.00	0.00	0.00
Ferric Sulfate	**(mg/L)**	0.00	0.00	0.00	25.00	25.00	25.00
Final pH	**(pH)**	7.01	6.94	7.04	7.10	6.90	7.36
Final Mn Diss	**(mg/L)**	0.09	0.13	0.12	0.11	0.06	0.09
Final Mn Total	**(mg/L)**	0.11	0.15	0.14	0.13	0.07	0.11
Final Fe Diss	**(mg/L)**	0.00	0.00	0.00	0.00	0.00	0.00
Final Fe Total	**(mg/L)**	0.02	0.04	0.07	0.04	0.03	0.04
Final Turbidty	**(NTU)**	0.69	0.78	1.09	1.66	1.60	1.01
Final TOC	**(mg/L)**	1.59	2.15	1.33	1.47	1.63	1.36
Final UV 254	**(abs.)**	0.022	0.026	0.029	0.031	0.027	0.026

APPENDIX D

D.1 ELEVATED PH PREFILTER CHLORINE TEST

Table 31. Elevated pH Prefilter Chlorine Jar Test 1

Configuration		Jar 1 pH 6.8	Jar 2 pH 6.8	Jar 3 pH 7.2	Jar 4 pH 7.2	Jar 5 pH 7.6	Jar 6 pH 7.6
Actual pH	**(pH)**	7.00	7.04	7.18	7.18	7.59	7.60
Temp	**(°C)**	24.5	24.5	24.5	24.6	24.6	24.6
Total Chlorine	**(mg/L)**	0.17	0.21	0.23	0.19	0.24	0.17
Raw TOC	**(mg/L)**	2.10	1.99	1.87	2.12	2.08	1.84
Raw UV 254	**(abs.)**	0.105	0.091	0.095	0.099	0.102	0.112
Mn Diss	**(mg/L)**	0.06	0.07	0.06	0.06	0.06	0.07
Mn Total	**(mg/L)**	0.06	0.08	0.06	0.07	0.06	0.07
Fe Diss	**(mg/L)**	0.00	0.00	0.00	0.00	0.00	0.00
Fe Total	**(mg/L)**	0.09	0.08	0.08	0.07	0.07	0.08
Total Chlorine	**(mg/L)**	0.16	0.20	0.21	0.19	0.20	0.14
Final pH	**(pH)**	7.29	7.35	7.43	7.44	7.71	7.76
Final TOC	**(mg/L)**	1.85	1.95	1.81	2.07	1.98	1.83
Final UV 254	**(abs.)**	0.072	0.080	0.084	0.099	0.068	0.078

Table 32. Elevated pH Prefilter Chlorine Bench Scale Test 2

Configuration		Jar 1 pH 8.0	Jar 2 pH 8.0	Jar 3 pH 8.4	Jar 4 pH 8.4	Jar 5 pH 8.8	Jar 6 pH 8.8
Actual pH	**(pH)**	8.03	7.75	8.38	8.42	8.80	8.78
Temp	**(°C)**	24.1	24.1	24.2	24.2	24.1	24.1
Total Chlorine	**(mg/L)**	0.24	0.18	0.23	0.19	0.18	0.20
Raw TOC	**(mg/L)**	2.15	2.02	1.90	2.08	2.18	2.12
Raw UV 254	**(abs.)**	0.094	0.102	0.087	0.085	0.092	0.103
Mn Diss	**(mg/L)**	0.07	0.06	0.07	0.06	0.07	0.06
Mn Total	**(mg/L)**	0.07	0.08	0.07	0.07	0.07	0.06
Fe Diss	**(mg/L)**	0.00	0.00	0.00	0.00	0.00	0.00
Fe Total	**(mg/L)**	0.08	0.06	0.07	0.07	0.09	0.04
Total Chlorine	**(mg/L)**	0.19	0.14	0.18	0.15	0.13	0.16
Final pH	**(pH)**	7.99	7.95	8.15	8.31	8.54	8.62
Final TOC	**(mg/L)**	2.12	1.85	1.72	2.17	2.01	2.12
Final UV 254	**(abs.)**	0.095	0.077	0.083	0.089	0.095	0.097

D.2 ELEVATED PH LIQUID PERMANGANATE TEST

Table 33. Elevated pH Prefilter Permanganate Bench Scale Test 1

Configuration		Jar 1 pH 6.8	Jar 2 pH 6.8	Jar 3 pH 7.2	Jar 4 pH 7.2	Jar 5 pH 7.6	Jar 6 pH 7.6
Actual pH	**(pH)**	7.02	6.98	7.17	7.18	7.58	7.60
Temp	**(°C)**	24.2	24.1	24.2	24.2	24.2	24.3
Raw TOC	**(mg/L)**	2.08	1.92	1.97	2.04	1.99	2.10
Raw UV 254	**(abs.)**	0.095	0.086	0.091	0.082	0.098	0.087
Mn Diss	**(mg/L)**	0.03	0.02	0.01	0.01	0.00	0.00
Mn Total	**(mg/L)**	0.13	0.13	0.14	0.13	0.14	0.15
Fe Diss	**(mg/L)**	0.00	0.00	0.00	0.00	0.00	0.00
Fe Total	**(mg/L)**	0.09	0.08	0.07	0.08	0.08	0.11
Final pH	**(pH)**	7.35	7.25	7.37	7.49	7.67	7.76
Final TOC	**(mg/L)**	2.05	1.91	1.78	1.89	2.00	2.03
Final UV 254	**(abs.)**	0.084	0.083	0.086	0.093	0.099	0.101

Table 34. Elevated pH Prefilter Permanganate Bench Scale Test 2

Configuration		Jar 1 pH 8.0	Jar 2 pH 8.0	Jar 3 pH 8.4	Jar 4 pH 8.4	Jar 5 pH 8.8	Jar 6 pH 8.8
Actual pH	**(pH)**	8.01	8.02	8.40	8.44	8.80	8.81
Temp	**(°C)**	24.2	24.2	24.2	24.2	24.3	24.3
Raw TOC	**(mg/L)**	2.01	1.95	2.13	2.12	1.94	1.97
Raw UV 254	**(abs.)**	0.087	0.098	0.085	0.093	0.108	0.097
Mn Diss	**(mg/L)**	0.00	0.01	0.01	0.00	0.01	0.00
Mn Total	**(mg/L)**	0.13	0.13	0.13	0.12	0.13	0.12
Fe Diss	**(mg/L)**	0.02	0.00	0.00	0.02	0.00	0.00
Fe Total	**(mg/L)**	0.13	0.10	0.06	0.10	0.10	0.07
Final pH	**(pH)**	7.94	8.01	8.21	8.34	8.73	8.85
Final TOC	**(mg/L)**	1.87	1.77	1.96	2.06	1.65	2.00
Final UV 254	**(abs.)**	0.075	0.087	0.086	0.098	0.103	0.097

APPENDIX E

E.1 PREFILTER CHLORINATION THM STUDY

E.1.1 Prefilter Chlorine Off Results

Table 35. Prefilter Chlorine Off: 2 March 2009

	Postfilter		Clearwell	
pH (pH)	6.83	6.80	8.08	8.06
Temp (°C)	7.0	7.2	11.6	11.4
Turbidity (NTU)	0.56	0.48	0.56	0.56
Free Cl2 (mg/L)	DND	DND	0.59	0.60
Total Cl2 (mg/L)	DND	DND	0.71	0.68
TOC (mg/L)	1.09	1.05	1.06	1.07
UV 254 (abs.)	0.025	0.024	0.019	0.022
THM (µg/L)	0.00		10.19	
THMFP7 (µg/L)	0.00		33.41	

Table 36. Prefilter Chlorine Off: 3 March 2009

	Postfilter		Clearwell	
pH (pH)	6.94	6.89	8.00	8.03
Temp (°C)	14.1	14.3	12.7	13.2
Turbidity (NTU)	0.80	0.82	0.86	0.86
Free Cl2 (mg/L)	DND	DND	0.65	0.66
Total Cl2 (mg/L)	DND	DND	0.69	0.72
TOC (mg/L)	1.08	1.09	1.26	1.30
UV 254 (abs.)	0.024	0.022	0.019	0.017
THM (µg/L)	0.00		10.39	
THMFP7 (µg/L)	0.00		22.65	

Table 37. Prefilter Chlorine Off: 27 March 2009

	Postfilter		Clearwell	
pH (pH)	6.65	6.64	8.49	8.47
Temp (°C)	4.5	4.5	10.5	10.5
Turbidity (NTU)	0.29	0.27	1.10	1.12
Free Cl2 (mg/L)	DND	DND	0.59	0.60
Total Cl2 (mg/L)	DND	DND	0.66	0.68
TOC (mg/L)	0.97	0.97	1.04	1.01
UV 254 (abs.)	0.014	0.014	0.010	0.011
THM (µg/L)	0.00		15.53	
THMFP7 (µg/L)	0.16		58.62	

Table 38. Prefilter Chlorine Off: 28 March 2009

	Postfilter		Clearwell	
pH (pH)	6.68	6.65	8.17	8.22
Temp (°C)	10.0	10.2	6.2	6.2
Turbidity (NTU)	1.10	1.14	1.62	1.52
Free Cl2 (mg/L)	DND	DND	0.72	0.69
Total Cl2 (mg/L)	DND	DND	0.79	0.74
TOC (mg/L)	1.01	0.99	1.02	1.00
UV 254 (abs.)	0.025	0.023	0.021	0.020
THM (µg/L)	0.00		18.98	
THMFP7 (µg/L)	0.19		48.95	

Table 39. Prefilter Chlorine Off: 22 April 2009

	Prefilter		Postfilter		Clearwell	
pH (pH)	6.97	6.97	6.85	6.91	8.31	8.39
Temp (°C)	19.3	19.4	18.0	18.2	14.7	14.7
Turbidity (NTU)	0.739	0.682	0.242	0.219	0.218	0.222
Free Cl2 (mg/L)	DND	DND	DND	DND	0.62	0.60
Total Cl2 (mg/L)	DND	DND	DND	DND	0.68	0.69
TOC (mg/L)	0.99	1.12	0.95	0.95	0.98	0.97
UV 254 (abs.)	0.009	0.011	0.010	0.008	0.014	0.010
THM (µg/L)			0.98		20.60	
THMFP7 (µg/L)			0.91		48.46	
THMFP14 (µg/L)			0.89		53.15	

Table 40. Prefilter Chlorine Off: 23 April 2009

	Prefilter		Postfilter		Clearwell	
pH (pH)	6.91	6.91	6.94	6.93	7.20	7.27
Temp (°C)	16.9	17.0	15.9	15.9	15.7	15.7
Turbidity (NTU)	0.539	0.523	0.474	0.419	0.292	0.304
Free Cl2 (mg/L)	DND	DND	DND	DND	0.66	0.65
Total Cl2 (mg/L)	DND	DND	DND	DND	0.72	0.72
TOC (mg/L)	1.04	1.14	1.02	0.99	1.08	1.28
UV 254 (abs.)	0.009	0.010	0.007	0.007	0.007	0.008
THM (µg/L)			0.81		17.01	
THMFP7 (µg/L)			0.79		54.43	
THMFP14 (µg/L)			0.79		68.12	

Table 41. Prefilter Chlorine Off: 18 June 2009

	Prefilter		Postfilter		Clearwell	
pH (pH)	6.87	6.84	6.93	6.98	8.27	8.27
Temp (°C)	23.3	23.3	23.5	23.4	23.9	24.0
Turbidity (NTU)	0.500	0.489	0.193	0.177	0.235	0.229
Free Cl2 (mg/L)	DND	DND	DND	DND	0.59	0.60
Total Cl2 (mg/L)	DND	DND	DND	DND	0.67	0.69
TOC (mg/L)	1.31	1.21	1.08	1.07	1.08	1.21
UV 254 (abs.)	0.040	0.037	0.022	0.023	0.010	0.011
THM (µg/L)			0.71		64.31	
THMFP7 (µg/L)			1.69		67.02	
THMFP14 (µg/L)			1.68		50.68	

Table 42. Prefilter Chlorine Off: 19 June 2009

	Prefilter		Postfilter		Clearwell	
pH (pH)	6.74	6.70	6.78	6.78	8.24	8.25
Temp (°C)	22.6	22.5	22.1	22.1	24.0	23.9
Turbidity (NTU)	0.701	0.685	0.189	0.192	0.481	0.399
Free Cl2 (mg/L)	DND	DND	DND	DND	0.68	0.68
Total Cl2 (mg/L)	DND	DND	DND	DND	0.74	0.77
TOC (mg/L)	1.23	1.14	1.16	1.12	1.11	1.06
UV 254 (abs.)	0.021	0.022	0.019	0.018	0.027	0.030
THM (µg/L)			0.68		61.77	
THMFP7 (µg/L)			0.65		61.38	
THMFP14 (µg/L)			0.11		60.69	

E.1.2 Prefilter Chlorine On Results

Table 43. Prefilter Chlorine On: 5 March 2009

	Postfilter		Clearwell	
pH (pH)	6.78	6.80	7.86	7.83
Temp (°C)	11.2	11.4	16.7	17.0
Turbidity (NTU)	0.28	0.28	0.68	0.70
Free Cl2 (mg/L)	0.22	0.24	0.66	0.65
Total Cl2 (mg/L)	0.40	0.32	0.69	0.71
TOC (mg/L)	1.10	1.12	1.13	1.09
UV 254 (abs.)	0.014	0.011	0.013	0.011
THM (µg/L)	2.10		20.32	
THMFP7 (µg/L)	4.81		43.80	

Table 44. Prefilter Chlorine On: 6 March 2009

	Postfilter		Clearwell	
pH (pH)	6.40	6.51	8.07	8.04
Temp (°C)	6.8	7.4	7.7	7.8
Turbidity (NTU)	0.61	0.59	0.69	0.66
Free Cl2 (mg/L)	0.36	0.35	0.56	0.49
Total Cl2 (mg/L)	0.48	0.49	0.62	0.58
TOC (mg/L)	1.09	1.08	1.14	1.11
UV 254 (abs.)	0.020	0.020	0.013	0.012
THM (µg/L)	1.81		15.64	
THMFP7 (µg/L)	3.44		33.15	

Table 45. Prefilter Chlorine On: 23 March 2009

	Postfilter		Clearwell	
pH (pH)	6.89	6.87	8.41	8.41
Temp (°C)	9.0	9.2	11.5	12.1
Turbidity (NTU)	0.50	0.52	0.50	0.49
Free Cl2 (mg/L)	0.09	0.08	0.65	0.65
Total Cl2 (mg/L)	0.24	0.25	0.73	0.73
TOC (mg/L)	0.98	0.99	1.04	1.02
UV 254 (abs.)	0.011	0.011	0.012	0.011
THM (µg/L)	4.04		14.89	
THMFP7 (µg/L)	4.75		48.41	

Table 46. Prefilter Chlorine On: 24 March 2009

	Postfilter		Clearwell	
pH (pH)	6.69	6.68	8.43	8.40
Temp (°C)	10.7	11.0	10.9	11.0
Turbidity (NTU)	1.02	1.00	0.43	0.50
Free Cl2 (mg/L)	0.19	0.18	0.80	0.80
Total Cl2 (mg/L)	0.27	0.27	0.82	0.82
TOC (mg/L)	0.97	0.98	1.04	1.03
UV 254 (abs.)	0.080	0.052	0.015	0.019
THM (µg/L)	3.74		15.60	
THMFP7 (µg/L)	5.76		31.49	

Table 47. Prefilter Chlorine On: 21 April 2009

	Prefilter		Postfilter		Clearwell	
pH (pH)	6.92	6.85	7.12	7.10	8.49	8.48
Temp (°C)	18.0	18.1	17.9	18.2	17.5	17.6
Turbidity (NTU)	0.462	0.455	0.540	0.552	0.433	0.408
Free Cl2 (mg/L)	0.33	0.35	0.06	0.09	0.61	0.58
Total Cl2 (mg/L)	0.40	0.39	0.12	0.16	0.67	0.68
TOC (mg/L)	1.52	1.12	1.02	1.03	0.98	1.07
UV 254 (abs.)	0.061	0.072	0.124	0.098	0.094	0.067
THM (µg/L)			7.19		25.20	
THMFP7 (µg/L)			9.69		42.53	
THMFP14 (µg/L)			9.53		41.68	

Table 48. Prefilter Chlorine On: 28 April 2009

	Prefilter		Postfilter		Clearwell	
pH (pH)	7.01	7.01	7.04	7.04	7.73	7.89
Temp (°C)	20.2	20.3	18.6	18.6	20.0	20.2
Turbidity (NTU)	0.832	0.912	0.702	0.655	0.312	0.299
Free Cl2 (mg/L)	0.19	0.17	0.13	0.11	0.67	0.73
Total Cl2 (mg/L)	0.34	0.39	0.15	0.16	0.78	0.77
TOC (mg/L)	1.07	1.12	1.02	1.00	1.02	1.00
UV 254 (abs.)	0.011	0.009	0.009	0.007	0.008	0.010
THM (µg/L)			5.29		21.10	
THMFP7 (µg/L)			8.00		40.54	
THMFP14 (µg/L)			10.71		45.30	

Table 49. Prefilter Chlorine On: 15 June 2009

	Prefilter		Postfilter		Clearwell	
pH (pH)	6.63	6.63	6.63	6.60	8.15	8.12
Temp (°C)	22.4	22.4	22.1	22.2	24.0	24.1
Turbidity (NTU)	0.672	0.699	0.272	0.270	0.275	0.281
Free Cl2 (mg/L)	0.19	0.15	0.09	0.07	0.61	0.60
Total Cl2 (mg/L)	0.39	0.40	0.10	0.12	0.73	0.71
TOC (mg/L)	1.24	1.31	1.36	1.31	1.44	1.16
UV 254 (abs.)	0.032	0.033	0.031	0.022	0.018	0.016
THM (µg/L)			9.60		50.79	
THMFP7 (µg/L)			12.75		81.73	
THMFP14 (µg/L)			9.07		52.37	

Table 50. Prefilter Chlorine On: 16 June 2009

	Prefilter		Postfilter		Clearwell	
pH (pH)	6.61	6.69	6.82	6.81	7.81	7.90
Temp (°C)	23.2	23.3	23.2	23.2	23.2	23.3
Turbidity (NTU)	0.721	0.704	0.360	0.360	0.374	0.370
Free Cl2 (mg/L)	0.46	0.42	0.05	0.04	0.70	0.71
Total Cl2 (mg/L)	0.56	0.57	0.06	0.06	0.74	0.74
TOC (mg/L)	1.12	1.16	1.04	1.08	1.07	1.06
UV 254 (abs.)	0.019	0.017	0.018	0.018	0.015	0.015
THM (µg/L)			10.93		60.49	
THMFP7 (µg/L)			13.12		96.78	
THMFP14 (µg/L)			10.82		49.51	

E.1.3 Additional Charts

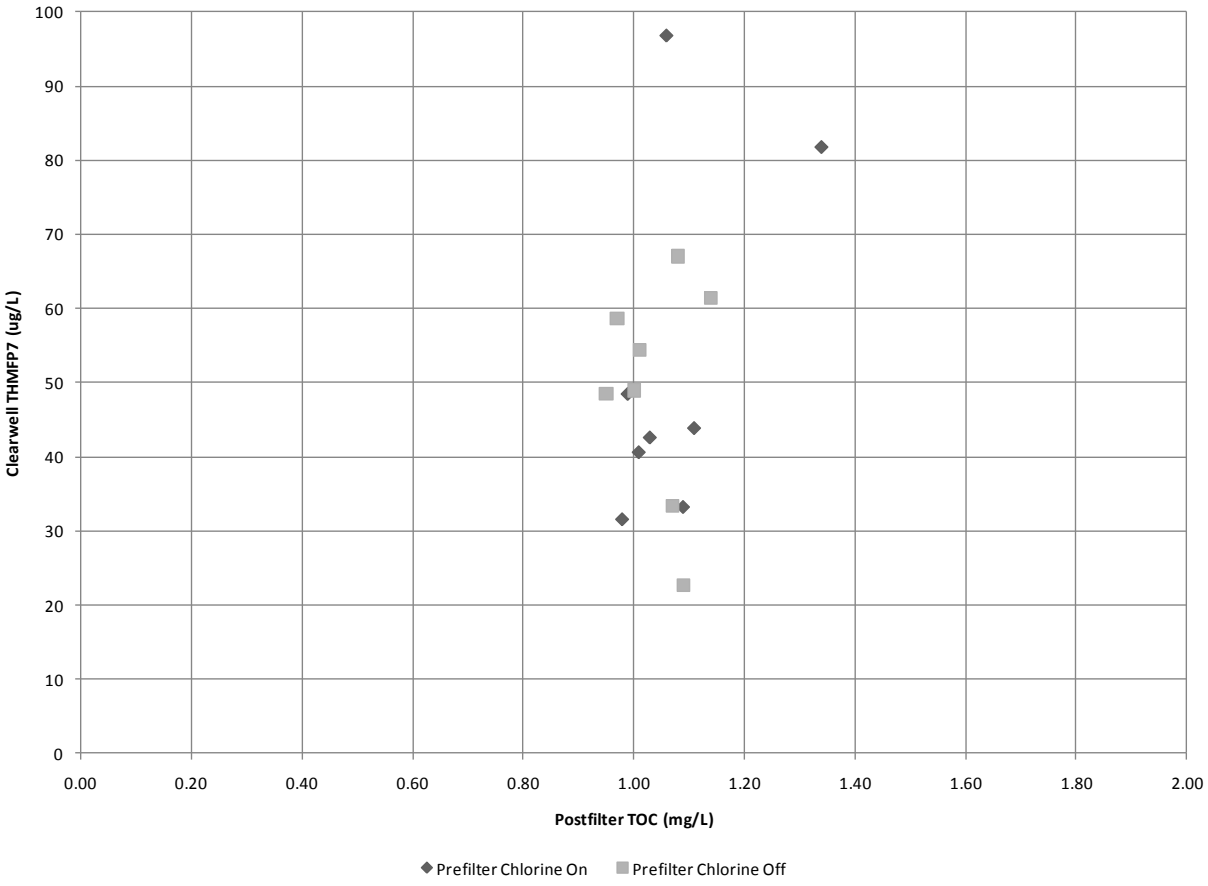

Figure 40. Postfilter TOC Levels and the Effects on Clearwell THMFP7 Plant-Scale Study

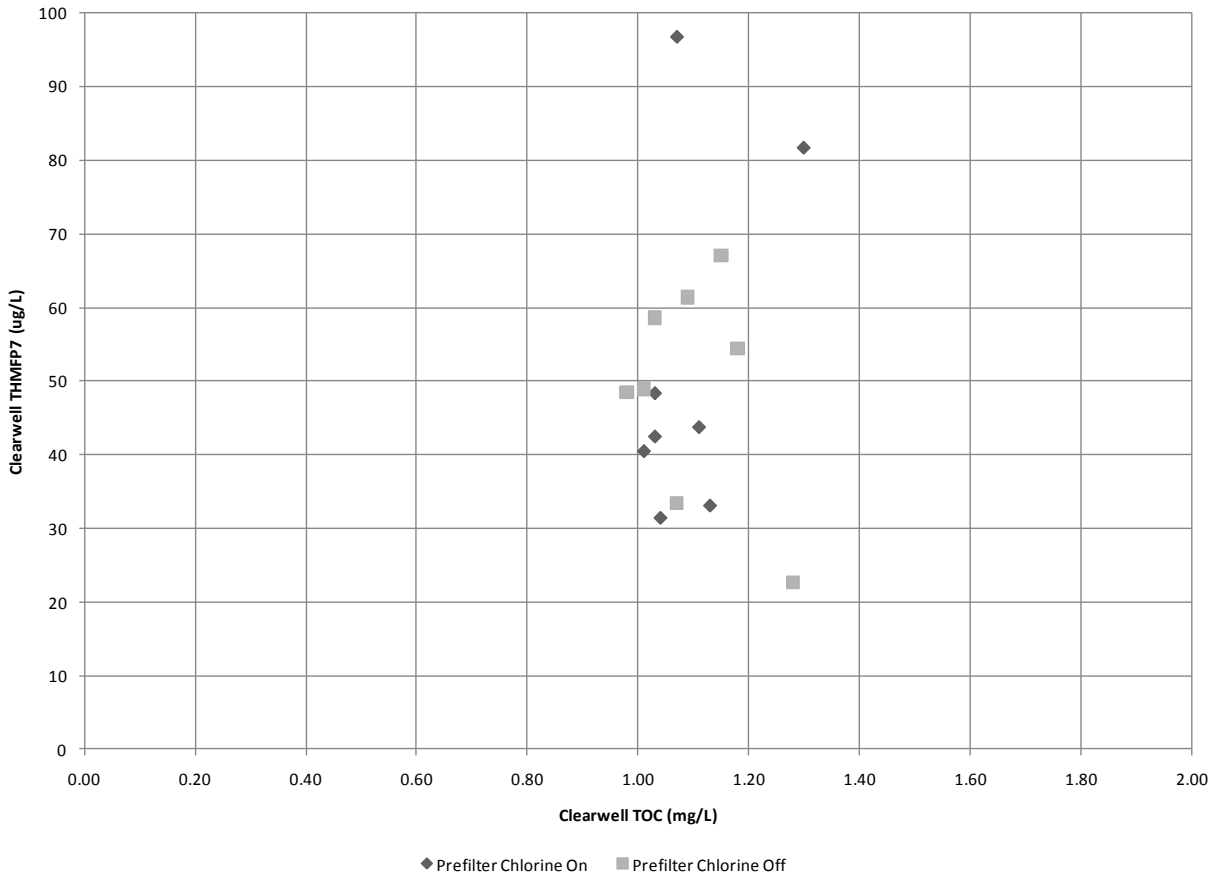

Figure 41. Clearwell TOC Levels and the Effects on Clearwell THMFP7 Plant-Scale Study

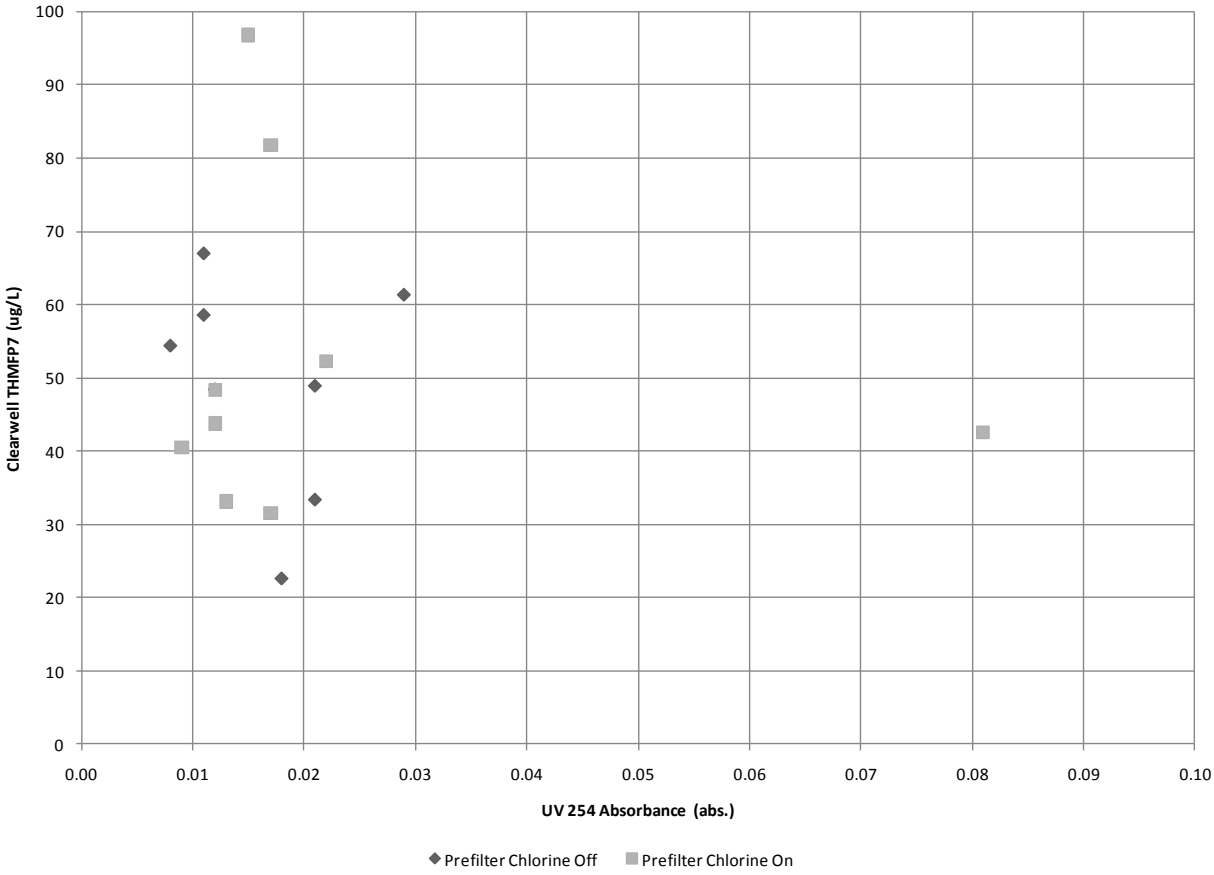

Figure 42. Clearwell UV 254 Absorbance and the Effects of Clearwell THMFP7 Plant-Scale Study

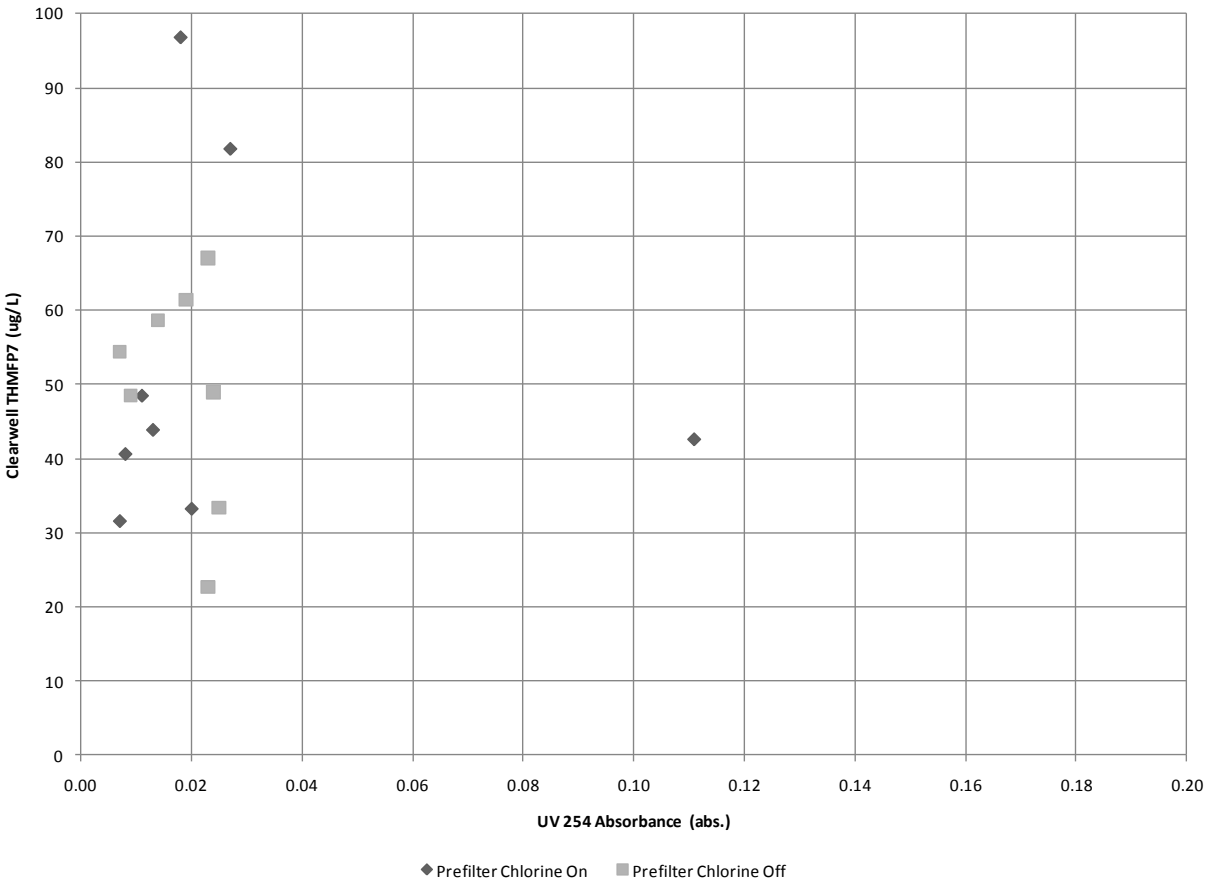

Figure 43. Postfilter UV 254 Absorbance and Effects on Clearwell THMFP7 Plant-Scale Study

APPENDIX F

F.1 CHLORINE SPIKE EXPERIMENTS

F.1.1 0.5 mg/L Chlorine Spike Experiment Data

Table 51. 0.5 mg/L Chlorine Spike Bench-Scale Study Using Plant Water

	Total Cl2 mg/L	THM ug/L
6/3/2009 10:45 AM Prefilter 1	0.33	4.05
6/3/2009 10:45 AM Prefilter 2	0.31	3.11
6/3/2009 10:45 AM PostFilter 1	0.36	3.89
6/3/2009 10:45 AM PostFilter 2	0.35	5.99
6/4/2009 12:00 PM Prefilter 1	0.34	3.61
6/4/2009 12:00 PM Prefilter 2	0.30	5.23
6/4/2009 12:50 PM PostFilter 1	0.18	4.91
6/4/2009 12:50 PM PostFilter 2	0.26	4.89

F.1.2 1.0 mg/L Chlorine Spike Experiment Data

Table 52. 1.0 mg/L Chlorine Spike Bench-Scale Study Using Plant Water

	Total Cl2 mg/L	THM ug/L
6/18/2009 9:00 AM Prefilter 1	0.88	5.22
6/18/2009 9:00 AM Prefilter 2	0.76	11.85
6/18/2009 11:00 AM PostFilter 1	0.49	7.08
6/18/2009 11:00 AM PostFilter 2	0.60	8.56
6/19/2009 12:00 PM Prefilter 1	0.79	9.27
6/19/2009 12:00 PM Prefilter 2	0.76	11.30
6/19/2009 2:00 PM PostFilter 1	0.48	5.68
6/19/2009 2:00 PM PostFilter 2	0.56	2.04

F.1.3 2.0 mg/L Chlorine Spike Experiment Data

Table 53. 2.0 mg/L Chlorine Spike Bench-Scale Study Using Plant Water

	Total Cl2 mg/L	THM ug/L
7/23/2009 10:00 AM Prefilter 1	0.09	43.23
7/23/2009 10:00 AM Prefilter 2	0.01	44.63
7/23/2009 12:00 PM PostFilter 1	0.03	38.87
7/23/2009 12:00 PM PostFilter 2	0.02	46.44
7/24/2009 1:00 PM Prefilter 1	0.02	41.51
1:00 PM 12:00 PM Prefilter 2	0.02	133.50
7/24/2009 3:00 PM PostFilter 1	0.02	77.69
7/24/2009 3:00 PM PostFilter 2	0.00	49.67

APPENDIX G

G.1 DISINFECTION BYPRODUCT PRECURSOR PLANT PROFILE

G.1.1 April 2009 Disinfection Byproduct Precursor Profile Plant-Scale Study

Table 54. April 2009 Disinfection Byproduct Precursor Profile Plant-Scale Study

Date	Time	Process	Time (hours)	TOC 1 (mg/L)	TOC 2 (mg/L)	TOC Average (mg/L)	Percent Reduction	UV254 1 (abs.)	UV 254 2 (abs.)	Average (abs.)	Percent Reduction
4/28/2009	**3pm**	**Raw Water**	0	2.12	2.28	2.20	--	0.056	0.062	0.059	--
4/28/2009	**5pm**	**Flume**	2	1.19	1.23	1.21	45%	0.035	0.038	0.037	38%
4/30/2009	**8am**	**Prefilter**	39	1.28	1.24	1.26	-2%	0.025	0.027	0.026	18%
4/30/2009	**10am**	**Postfilter**	2	1.13	1.17	1.15	5%	0.017	0.018	0.018	14%
4/30/2009	**6pm**	**Clear well**	8	1.2	1.15	1.18	-1%	0.006	0.006	0.006	19%

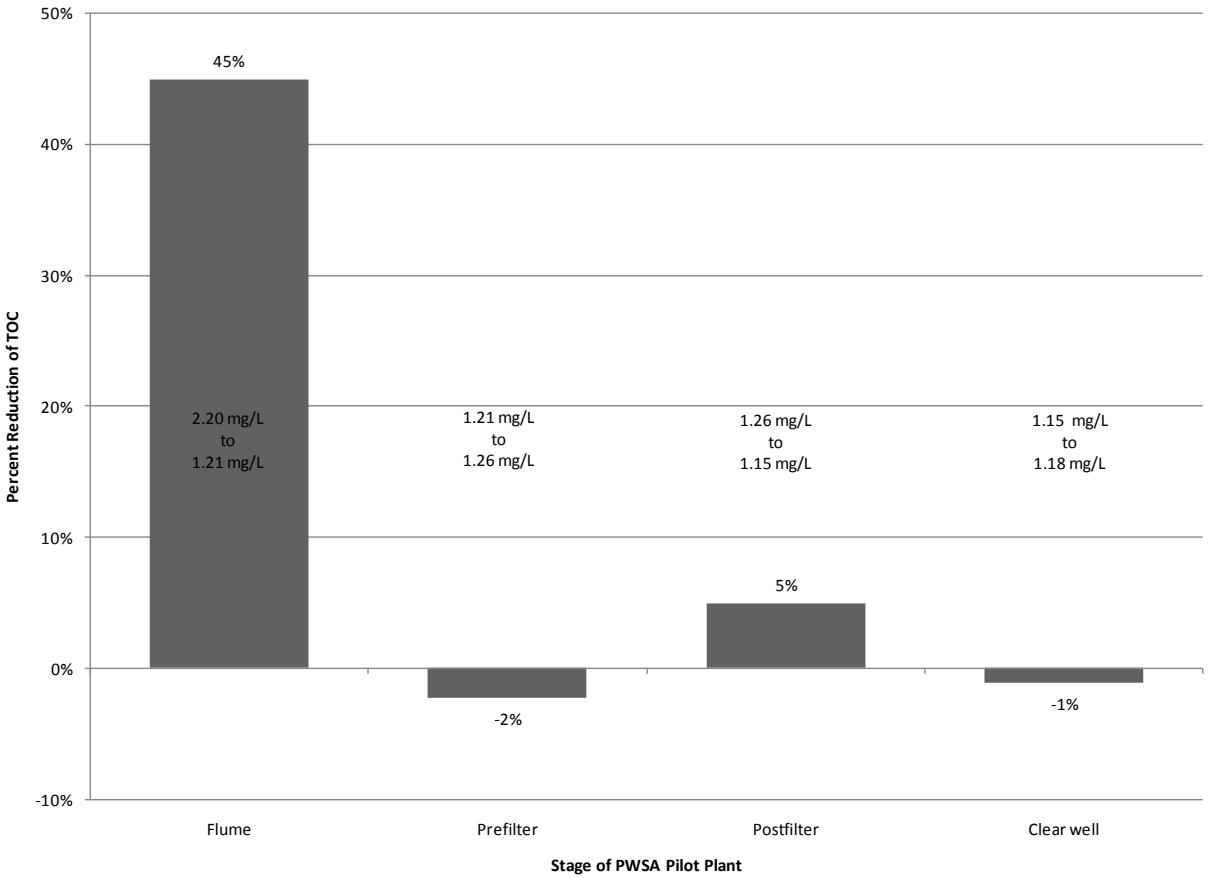

Figure 44. Unit Process Percent Reduction of TOC Week of April 27, 2009 Plant-Scale Study

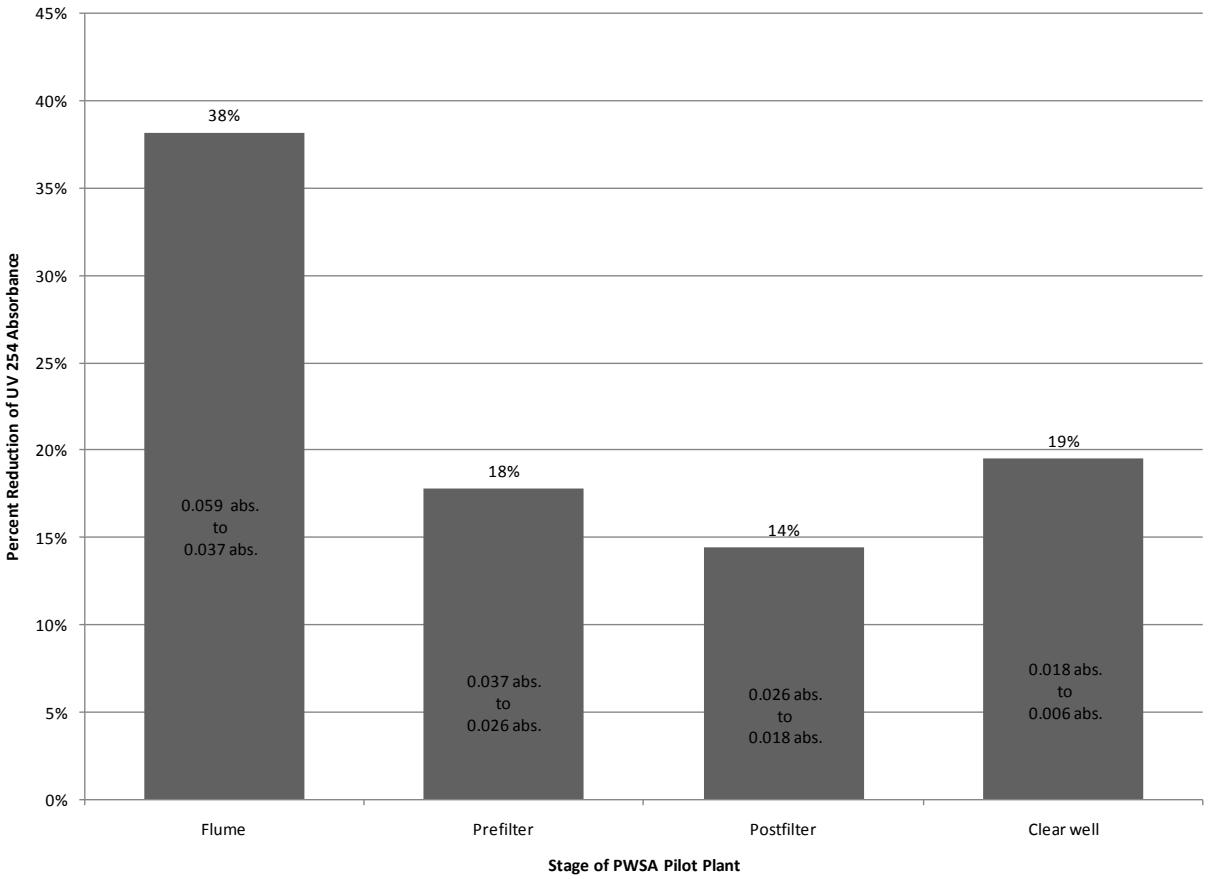

Figure 45. Unit Process Reduction of UV 254 Absorbance Week of April 27, 2009 Plant-Scale Study

G.1.2 July 2009 Disinfection Byproduct Precursor Profile Plant-Scale Study

Table 55. July 2009 Disinfection Byproduct Precursor Profile Plant-Scale Study

Date	Time	Process	Time (hours)	TOC 1 (mg/L)	TOC 2 (mg/L)	TOC Average (mg/L)	Percent Reduction	UV254 1 (abs.)	UV 254 2 (abs.)	Average (abs.)	Percent Reduction
7/22/2009	3pm	Raw Water	0	3.10	3.12	3.11	--	0.160	0.163	0.162	--
7/22/2009	5pm	Flume	2	1.79	1.69	1.74	44%	0.093	0.095	0.094	42%
7/24/2009	8am	Prefilter	39	1.61	1.70	1.66	3%	0.027	0.027	0.027	41%
7/24/2009	10am	Postfilter	2	1.57	1.53	1.55	3%	0.015	0.017	0.016	7%
7/24/2009	6pm	Clear well	8	1.60	1.61	1.61	-2%	0.009	0.010	0.010	4%

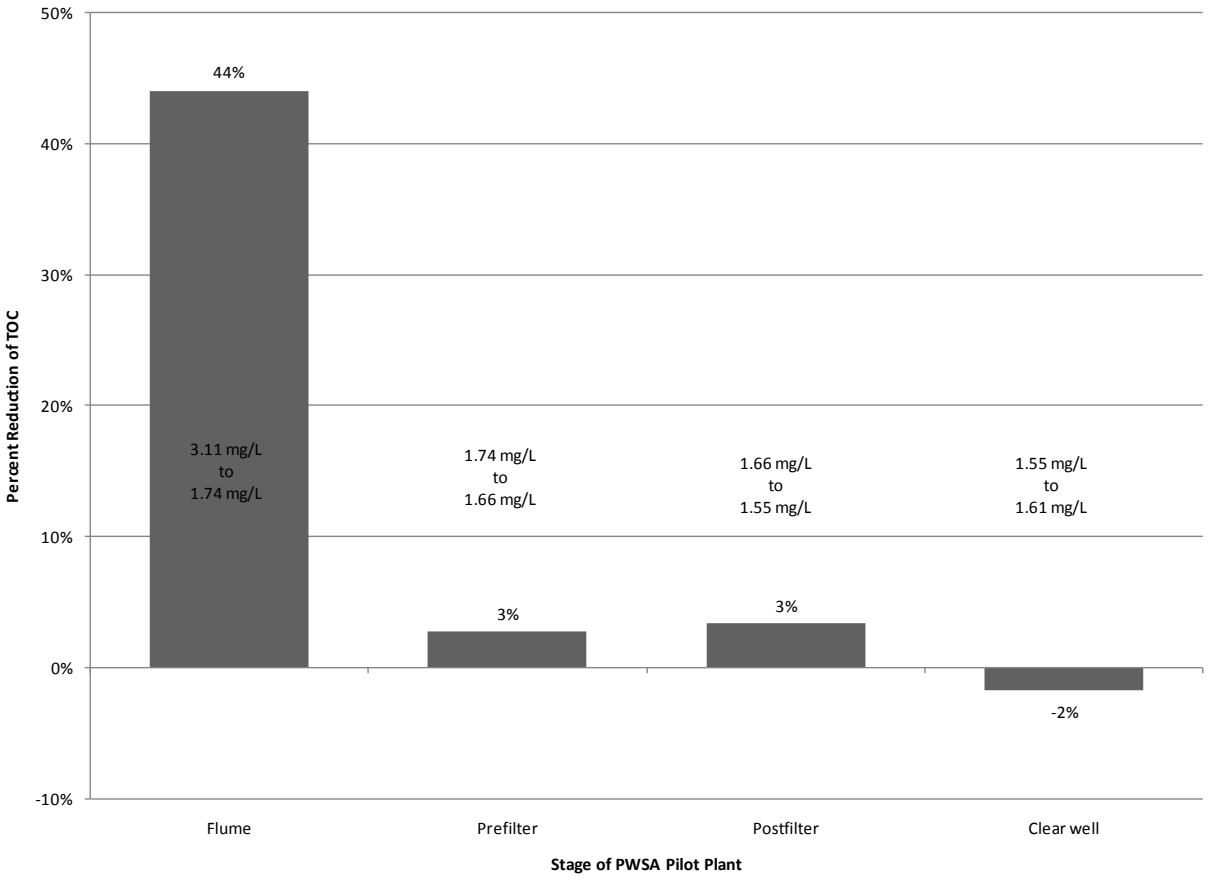

Figure 46. Unit Process Percent Reduction of TOC Week of July 20, 2009 Plant-Scale Study

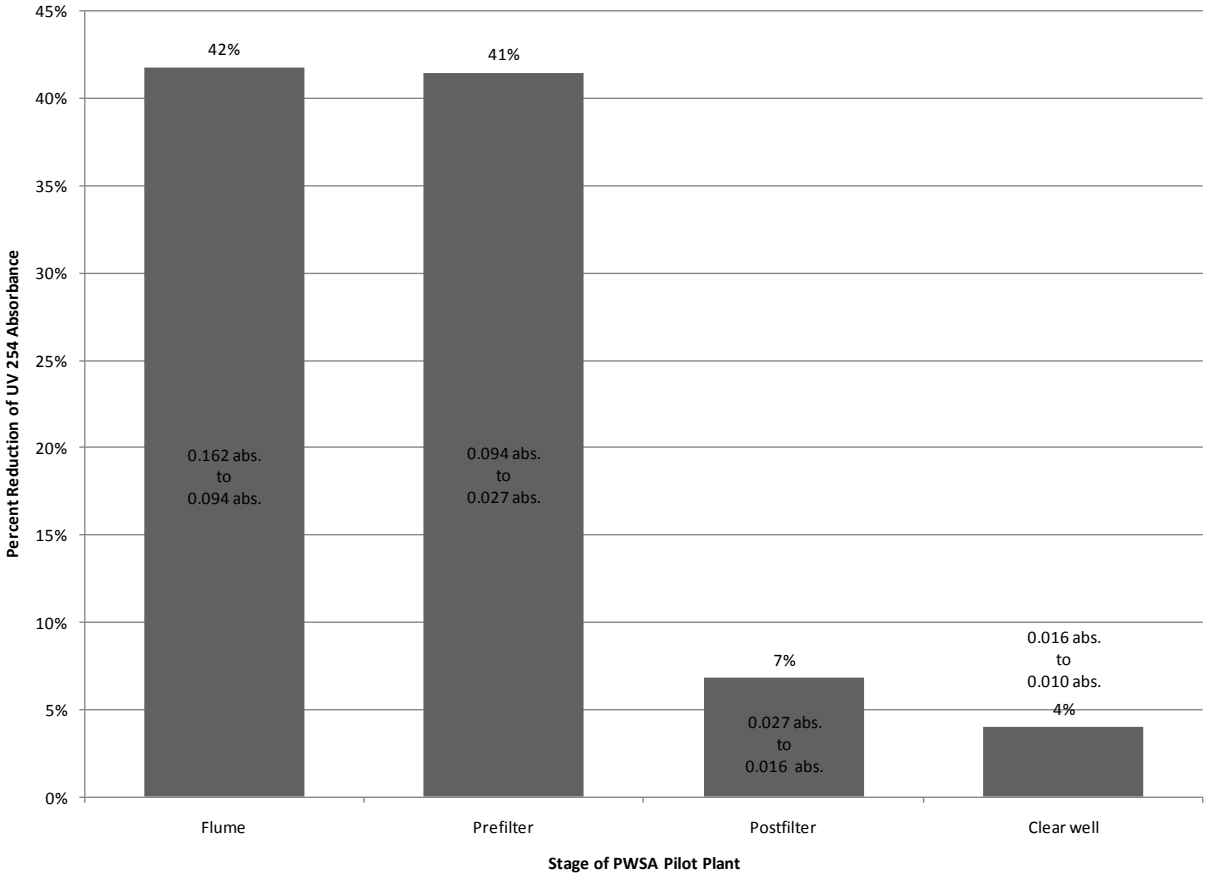

Figure 47. Unit Process Percent Reduction of UV 254 Absorbance Week of July 20, 2009 Plant-Scale Study

APPENDIX H

H.1 LIQUID PERMANGANATE PILOT STUDY

H.1.1 Pilot Plant Data 0.05 and 0.10 mg/L Test

Table 56. Liquid Permanganate 0.05 and 0.10 mg/L Dose Pilot-Scale Study

	Date		7/27/2009	7/28/2009	7/30/2009	7/31/2009
Flow	**Condition**		**PFC ON**	**PFC OFF**	**PFC OFF MnO4 0.05 mg/L**	**PFC OFF MnO4 0.10 mg/L**
	Flow	**gpm**	0.20	0.20	0.20	0.20
	Loading Rate	**gpm/sq. ft**	1.02	1.02	1.02	1.02
Prefilter	**Pressure**	**PSI**	1.0	1.0	1.0	1.0
	Turbidity	**NTU**	1.69	2.03	1.93	1.85
	Free Cl2	**mg/L**	0.30	DND	DND	DND
	Total Cl2	**mg/L**	0.46	DND	DND	DND
	Mn Diss	**mg/L**	0.03	0.05	0.05	0.06
	Mn Total	**mg/L**	0.07	0.05	0.05	0.08
	Fe Diss	**mg/L**	0.00	0.00	0.01	0.00
	Fe Total	**mg/L**	0.10	0.09	0.11	0.12
	TOC	**mg/L**	1.32	1.33	1.50	1.62
	UV 254	**abs.**	0.051	0.039	0.084	0.061
Posfilter	**Pressure**	**PSI**	4.0	4.0	4.0	4.0
	Turbidity	**NTU**	0.10	0.12	0.18	0.29
	Free Cl2	**mg/L**	0.08	DND	DND	DND
	Total Cl2	**mg/L**	0.21	DND	DND	DND
	Mn Diss	**mg/L**	0.00	0.04	0.04	0.07
	Mn Total	**mg/L**	0.00	0.05	0.05	0.07
	Fe Diss	**mg/L**	0.00	0.00	0.00	0.00
	Fe Total	**mg/L**	0.00	0.00	0.00	0.00
	TOC	**mg/L**	1.25	1.12	1.15	1.41
	UV 254	**abs.**	0.039	0.018	0.060	0.044
Reduction	**TOC**	**mg/L**	5%	16%	23%	13%
	UV 254	**abs.**	24%	54%	29%	28%
	Mn Diss	**mg/L**	100%	20%	20%	-17%
	Mn Total	**mg/L**	100%	0%	0%	13%

H.1.2 Pilot Plant Data 0.15 and 0.20 mg/L Test

Table 57. Liquid Permanganate 0.15 and 0.20 mg/L Dose Pilot-Scale Study

	Date		7/21/2009	7/22/2009	7/23/2009	7/24/2009
Flow	**Condition**		**PFC ON**	**PFC OFF**	**PFC OFF MnO4 0.20 mg/L**	**PFC OFF MnO4 0.15 mg/L**
	Flow	**gpm**	0.20	0.20	0.20	0.20
	Loading Rate	**gpm/sq. ft**	1.02	1.02	1.02	1.02
Prefilter	**Pressure**	**PSI**	1.0	1.0	1.0	1.0
	Turbidity	**NTU**	1.89	2.21	2.41	1.65
	Free Cl2	**mg/L**	0.22	DND	DND	DND
	Total Cl2	**mg/L**	0.51	DND	DND	DND
	Mn Diss	**mg/L**	0.03	0.05	0.06	0.07
	Mn Total	**mg/L**	0.03	0.05	0.09	0.07
	Fe Diss	**mg/L**	0.00	0.06	0.00	0.07
	Fe Total	**mg/L**	0.11	0.07	0.08	1.03
	TOC	**mg/L**	2.67	1.89	2.16	1.83
	UV 254	**abs.**	0.042	0.034	0.045	0.083
Posfilter	**Pressure**	**PSI**	4.0	4.0	4.0	4.0
	Turbidity	**NTU**	0.15	0.09	0.19	0.31
	Free Cl2	**mg/L**	0.02	DND	DND	DND
	Total Cl2	**mg/L**	0.23	DND	DND	DND
	Mn Diss	**mg/L**	0.00	0.03	0.05	0.04
	Mn Total	**mg/L**	0.00	0.05	0.07	0.05
	Fe Diss	**mg/L**	0.00	0.00	0.00	0.00
	Fe Total	**mg/L**	0.01	0.04	0.02	0.03
	TOC	**mg/L**	1.83	1.66	1.47	1.60
	UV 254	**abs.**	0.018	0.032	0.033	0.019
Reduction	**TOC**	**mg/L**	31%	12%	32%	13%
	UV 254	**abs.**	57%	6%	27%	77%
	Mn Diss	**mg/L**	100%	40%	17%	43%
	Mn Total	**mg/L**	100%	0%	22%	29%

H.1.3 Pilot Plant Data 0.25 mg/L Test

Table 58. Liquid Permanganate 0.25 mg/L Dose Pilot-Scale Study

	Date		6/15/2009	6/16/2009	6/18/2009	6/19/2009
Flow	**Condition**		**PFC ON**	**PFC ON**	**PFC OFF MnO4 0.25 mg/L**	**PFC OFF MnO4 0.25 mg/L**
	Flow	**gpm**	0.20	0.25	0.20	0.20
	Loading Rate	**gpm/sq. ft**	1.02	1.27	1.02	1.02
Prefilter	**Pressure**	**PSI**	1.0	1.0	1.0	1.0
	Turbidity	**NTU**	2.46	5.81	3.38	1.62
	Free Cl2	**mg/L**	0.29	0.33	DND	DND
	Total Cl2	**mg/L**	0.36	0.49	DND	DND
	Mn Diss	**mg/L**	0.04	0.03	0.08	0.08
	Mn Total	**mg/L**	0.07	0.09	0.13	0.10
	Fe Diss	**mg/L**	0.02	0.00	0.00	0.00
	Fe Total	**mg/L**	1.30	2.09	1.33	0.65
	TOC	**mg/L**	1.35	1.37	1.43	1.55
	UV 254	**abs.**	0.028	0.032	0.072	0.038
Posfilter	**Pressure**	**PSI**	4.0	4.0	4.0	4.0
	Turbidity	**NTU**	0.13	0.10	0.33	0.62
	Free Cl2	**mg/L**	0.09	0.06	DND	DND
	Total Cl2	**mg/L**	0.13	0.10	DND	DND
	Mn Diss	**mg/L**	0.00	0.00	0.03	0.03
	Mn Total	**mg/L**	0.00	0.01	0.03	0.05
	Fe Diss	**mg/L**	0.00	0.00	0.00	0.01
	Fe Total	**mg/L**	0.00	0.00	0.01	0.01
	TOC	**mg/L**	1.24	1.28	1.11	1.34
	UV 254	**abs.**	0.027	0.022	0.059	0.021
Reduction	**TOC**	**mg/L**	8%	7%	22%	14%
	UV 254	**abs.**	4%	31%	18%	45%
	Mn Diss	**mg/L**	100%	100%	63%	63%
	Mn Total	**mg/L**	100%	89%	77%	50%

H.1.4 Pilot Plant Data 2.50 mg/L Test

Table 59. Liquid Permanganate 2.50 mg/L Dose Pilot-Scale Study

	Date		6/1/2009	6/2/2009	6/3/2009	6/4/2009
Flow	**Condition**		**PFC ON**	**PFC ON**	**PFC OFF**	**PFC OFF MnO4 2.50 mg/L**
	Flow	**gpm**	0.20	0.20	0.20	0.20
	Loading Rate	**gpm/sq. ft**	1.02	1.02	1.02	1.02
Prefilter	**Pressure**	**PSI**	0.50	0.0	0.2	0.2
	Turbidity	**NTU**				
	Free Cl2	**mg/L**	0.37	0.31	DND	DND
	Total Cl2	**mg/L**	0.49	0.47	DND	DND
	Mn Diss	**mg/L**	0.06	0.05	0.15	0.09
	Mn Total	**mg/L**	0.28	0.13	0.16	0.10
	Fe Diss	**mg/L**	0.06	0.06	0.00	0.01
	Fe Total	**mg/L**	6.39	2.69	1.23	1.15
	TOC	**mg/L**	1.51	1.31	1.35	1.47
	UV 254	**abs.**	0.14	0.125	0.074	0.057
Posfilter	**Pressure**	**PSI**	3.00	2.8	3.0	3.0
	Turbidity	**NTU**				
	Free Cl2	**mg/L**	0.18	0.04	DND	DND
	Total Cl2	**mg/L**	0.21	0.07	DND	DND
	Mn Diss	**mg/L**	0.04	0.07	0.16	0.07
	Mn Total	**mg/L**	0.04	0.08	0.17	0.08
	Fe Diss	**mg/L**	0.00	0.04	0.00	0.00
	Fe Total	**mg/L**	0.00	0.04	0.00	0.00
	TOC	**mg/L**	1.28	1.15	1.15	1.22
	UV 254	**abs.**	0.02	0.015	0.090	0.015
Reduction	**TOC**	**mg/L**	0.15	12%	15%	17%
	UV 254	**abs.**	0.83	88%	-22%	74%
	Mn Diss	**mg/L**	0.33	-40%	-7%	22%
	Mn Total	**mg/L**	0.86	38%	-6%	20%

H.1.5 Note

Some data that was collected in the Liquid Permanganate Pilot Study was not used in the graphs in section 6.2.3. due to poor plant conditions. There was extensive maintenance being performed on the rapid mixers and flocculating basins. On certain occasions the iron and manganese concentration in the pilot plant would be 30 times greater than the actual plant. For this reason, data was omitted in the trend graphs. The complete data for the pilot plant is in sections G.1.1. through G.1.4.

APPENDIX I

I.1 PILOT-PLANT PICTURES

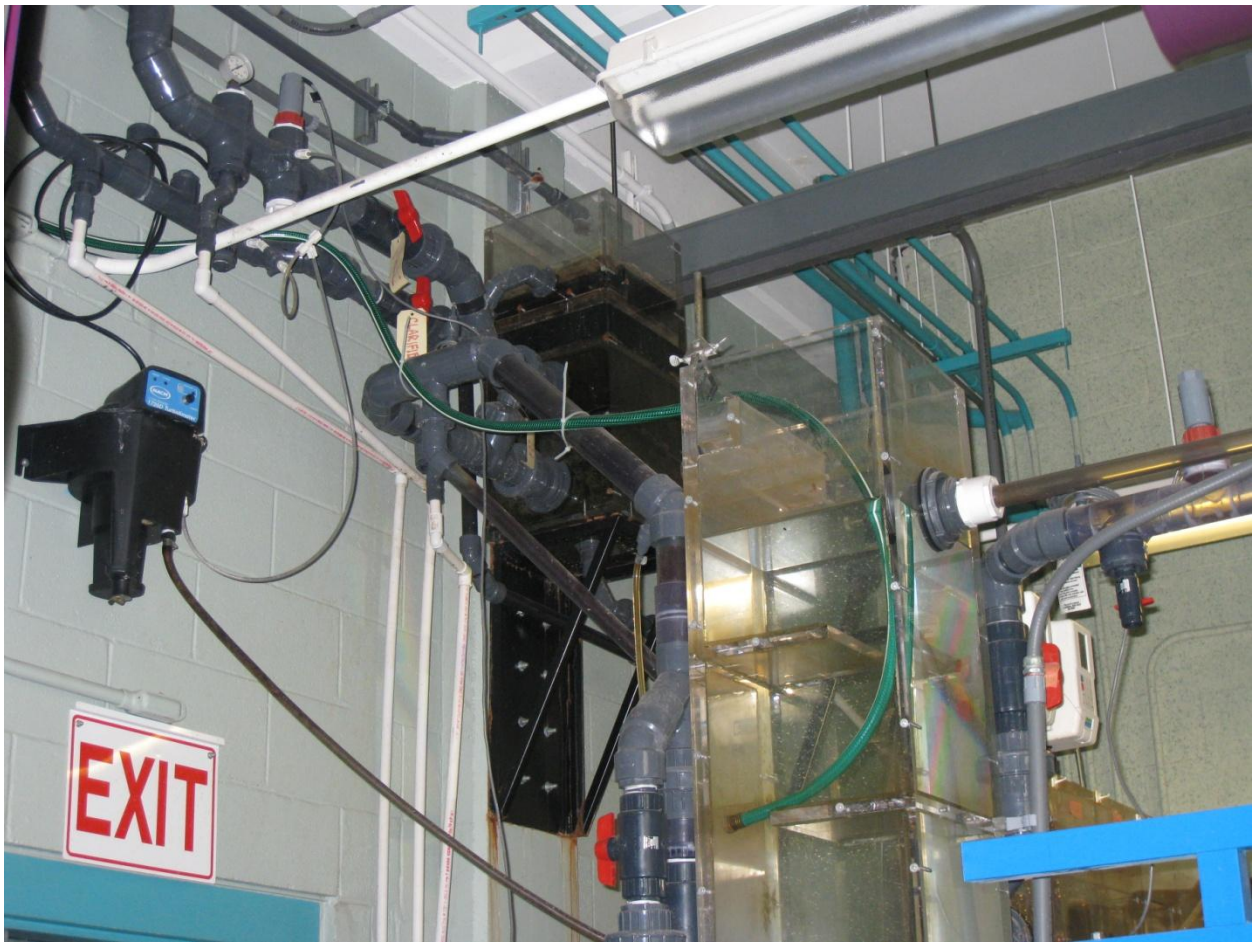

Figure 48. PWSA Pilot-Plant River Water Intake

Figure 49. PWSA Pilot-Plant Chemical Mix and Rapid Mix Unit Process

Figure 50. PWSA Pilot-Plant Flocculation Unit Process

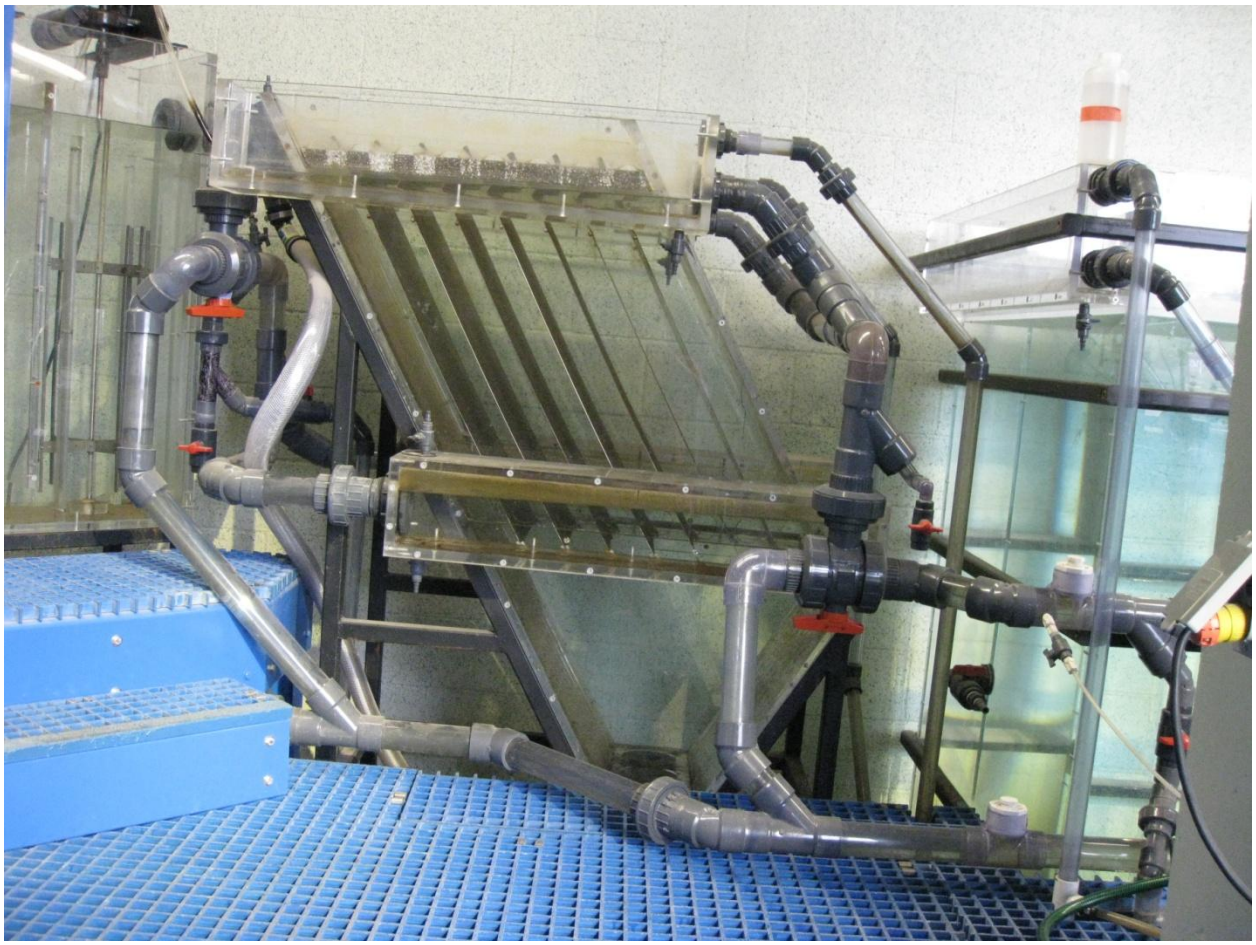

Figure 51. PWSA Pilot-Plant Primary Sedimentation with Parallel Plate Settlers

Figure 52. PWSA Pilot-Plant Secondary Sedimentation Basin

Figure 53. PWSA Pilot-Plant Sodium Permanganate Dosing System for Prefilter Permanganate Pilot-Scale Studies

Figure 54. PWSA Pilot-Plant Top Half of the Dual-Media Filters

Figure 55. PWSA Pilot-Plant Bottom Half of the Dual-Media Filters

Figure 56. PWSA Pilot-Plant Backwash Basin and Pump for Dual-Media Filters

BIBLIOGRAPHY

Alzheimer's Society. (2008, September). *Alzheimer's Society*. Retrieved July 2, 2009, from Aluminum and Alzheimer's Disease: http://alzheimers.org.uk/factsheet/406

AWWA and EES. (2002). Finished Water Storage Facilities. *USEPA Office of Ground Water and Drinking Water Standards and Risk Management Division* .

Bitton, G. (2005). *Wastewater Microbiology.* Hoboken: John Wiley & Son Inc.

Connick, R. E. (1947, June). The Interacton of Hydrogen Peroxide and Hypochlorous Acid in Acidic Solutions Containing Chloride Ion. *Journal of the American Chemical Society* , 1509-1514.

Daley, C. (2007). *Pittsburgh Water and Sewer Authority Comprehensive Distribution System Flouride Tracer Study.* Pittsburgh, PA: University of Pittsburgh.

El-Shafy, M. A., & Grunwald, A. (2000). THM Formation in Water Supply in South Bohemia, Czech Republic. *Water Research , 34* (13), 3453-3459.

Flaherty, T. (2002, December 31). *Annual Financial Report of the City of Pittsburgh*. Retrieved June 22, 2009, from Pittsburgh's Controllers Office: http://www.city.pittsburgh.pa.us/co/assets/City_of_Pgh_CAFR_Final_2002.pdf

FMC Corporation. (2008, June 3). *Material Safety Data Sheet Hydrogen Peroxide.* Retrieved June 10, 2009, from FMC Corporation: http://msds.fmc.com/msds/100000010225-MSDS_US-E.pdf

Kavanough M. C., T. A. (1980). An empirical kinetic model of THM formation: applications to meet the proposed THM standards. *Jouranal of the American Water Works Association , 72*, 578-582.

Makower, B., & Bray, W. C. (1933). The Rate of Oxidation of Hydrogen Peroxide by Chlorine in the Presence of Hydrochloric Acid. *Journal of American Chemical Society* , 4765.

MWH. (2005). *Water Treatment: Principles and Design* (2 ed.). Hoboken, NJ: John Wiley & Sons.

Nguyen-Tang, L. (2002, August 19). *Newsletter of the SFSU College of Science and Engineering Alumni Chapter*. Retrieved July 20, 2009, from San Francisco State University: http://www.sfsu.edu/~science/newsletters/fall2001/equip1.jpg

PADEP. (2004). *Title 25 Environmental Protection.* Retrieved June 22, 2009, from Safe Drinking Water: http://www.pacode.com/secure/data/025/chapter109/chap109toc.html

PWSA. (2006). *Finished Metals Analysis 2005.* Pittsburgh, PA: PWSA.

PWSA. (2000). *PWSA Pilot Plant Operation and Maintenance Manual.* Pittsburgh: PWSA.

Rayner-Canham, G. (1996). *Descriptive Inorganic Chemistry.* New York: Freeman.

Satterfield, P. Z. (2005). *Tech Brief: Jar Testing*. Retrieved June 25, 2009, from West Virginia University: http://www.nesc.wvu.edu/pdf/dw/publications/ontap/2009_tb/jar_testing_DWFSOM73.pdf

Sommerfeld, E. O. (1999). *Iron and Manganese Removal Handbook.* Denver, CO: American Water Works Association.

States, S. (2009, July 15). Water Quality Manager of PWSA. (D. Weakley, Interviewer)

States, S., Tomko, R., Scheuring, M., & Casson, L. (2002). Enhanced Coagulation and Removal of Cryptosporidium. *AWWA , 94* (11), 1-11.

U.S. Peroxide. (2005, March 21). *Introduction to Hydrogen Peroxide*. Retrieved July 2, 2009, from Hydrogen Peroxide Online: http://www.h2o2.com

USEPA. (1999, May). *Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual.* Retrieved July 1, 2009, from United States Environmental Protection Agency: http://www.epa.gov/OGWDW/mdbp/coaguide.pdf

USEPA. (2009, March 17). *Safe Drinking Water Act*. Retrieved July 1, 2009, from United States Environmental Protection Agency: http://www.epa.gov/OGWDW/sdwa/basicinformation.html

USEPA. (2006, November 28). *Stage 1 Disinfectants and Disinfection Byproducts Rule*. Retrieved February 09, 2009, from http://www.epa.gov/OGWDW/mdbp/dbp1.html

USEPA. (2007, June 29). *Stage 2 Disinfectants and Disinfection Byproduct Rule (Stage 2 DBP rule).* Retrieved February 09, 2009, from http://www.epa.gov/ogwdw/disinfection/stage2/basicinformation.html#questions

Westphal, K. S., Chapra, S. C., & Sung, W. (2004, June). Modeling TOC and UV-254 Absorbance for Reservoir Planning and Operation. *Journal of the American Water Resources Association* , 795-809.